PHOSPHORUS DYNAMICS IN AN ACIDIC, SOFT-WATER FLORIDA LAKE

by

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TABLE OF CONTENTS

Abstract of Dissertation Presented to the Graduate Council of
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Laboratory and *in situ* experiments as well as historical data were used to characterize phosphorus dynamics in acidic, soft-water McCloud Lake, Florida, and to evaluate the effect of acidification on phosphorus cycling processes. McCloud presently exhibits nutrient and chlorophyll-*a* concentrations typical of oligotrophic Florida lakes. A 15-year pH decline (4.85 to 4.55) has not been accompanied by significant changes in TP, chlorophyll-*a*, or nitrogen to phosphorus ratios, which indicate phosphorus-limited primary production.

Total phosphorus shows maxima during late spring and summer, and variations appeared to be related to rainfall patterns and lake levels during 1980–1982. Atmospheric phosphorus deposition is near the loading rate necessary to maintain mesotrophic conditions, which suggests that low pH may contribute to the low TP in McCloud Lake. Rooted submergent macrophytes represent an in-lake storage of

phosphorus that is approximately 2.5 times the average water column phosphorus storage, although the macrophytes do not appear to compete with phytoplankton for SRP.

In situ littoral and open-water mesocosm data indicated that acidification (from 4.6 to 3.7) does lead to reduced water column TP levels, although the trends were not consistent in the open-water enclosures, which were not connected to the sediments. No relation was seen between pH and rates of phosphorus uptake by planktonic communities, and pH did not affect the activity of extracellular acid phosphatase enzymes in laboratory microcosms.

The amount of SRP released from decomposing submersed macrophytes was independent of pH (over the range 3.7 to 5.5) after 227 days of aerobic dark incubation, although initial rates of release were somewhat faster at the lowest pH. These experiments showed that acidification does not inhibit phosphorus release during decomposition of aquatic plants.

Effects of pH on surface charge characteristics and SRP speciation cause sediment adsorption of SRP to vary with pH. Maximum SRP adsorption occurred near pH 4.7, although there was little variation between pH 5.0 and 3.5. However, significant decrease in SRP adsorption at pH $>$ 5 indicates that this mechanism may contribute to the observed trend of low TP in acidic lakes. This effect would be greatest over the pH range 7.0 to 5.0, and further acidification of lakes near the pH of McCloud Lake would have little effect on SRP adsorption.

CHAPTER 1
INTRODUCTION

Background

Acidic precipitation is considered to have pH < 5.6, which is the pH of pure water in equilibrium with atmospheric CO_2 (Likens et al. 1979). Sulfur and nitrogen oxides from anthropogenic emissions (and from natural sources to a smaller extent) react with water vapor in the atmosphere to form sulfuric acid and nitric acid. The return of these acids to the earth with rainfall is known as acid precipitation, or acid rain. However, dryfall of particulates and gaseous deposition can also contribute significant amounts of acid to the earth's surface. Therefore, acid precipitation generally refers to rainfall acidity, while acid deposition includes wetfall, gaseous, and dryfall acidity.

Acid precipitation was described in England as early as 1852 and was linked to changes in water chemistry by Gorham in the 1950's, although it was not recognized as a widespread and serious threat to aquatic and terrestrial ecosystems until the 1960's and 1970's (Cowling 1982). The chemical and biological changes associated with acidification of Scandinavian lakes and streams generated intense political and scientific interest in determining the sources, extent and effects of atmospheric acidity. In North America, acid precipitation has been documented in the northeastern United States and southeastern Canada, in the southeastern U.S. (including Florida), and in the Rocky

Mountains. Effects of acid deposition on aquatic and terrestrial ecosystems are difficult to demonstrate conclusively, and the problem of differentiating between long-term trends in natural processes and short-term changes caused by relatively recent increases in atmospheric acidity remains a controversial issue.

Acid deposition has been implicated in accelerated erosion of buildings, human health problems including cancer, forest decline, decreased agricultural yields, and acidification of poorly buffered surface waters. Perhaps the most dramatic effect of aquatic acidification has been the elimination of trout populations from some temperate lakes and streams. Other aquatic effects have been inferred from surveys of lakes over a range of pH values.

Regional studies have shown similarities in the chemistry and biology of acidic lakes from different geographic areas. Phytoplankton and zooplankton assemblages tend to become more simplified with decreasing lake pH, and similar groups of species are found in acidic lakes of Scandinavia and temperate North America (Sprules 1975; NRCC 1981; Confer et al. 1983). Grahn et al. (1974) found that acidic lakes in Scandinavia showed greater transparency and lower chlorophyll-a and macrophyte abundance than non-acidic lakes. They hypothesized that acidification causes an "oligotrophication" process in which reduced rates of organic matter decomposition and nutrient recycling lead to lower rates of primary production. Surveys in Canada and the northeastern U.S. have shown similar trends in transparency, chlorophyll-a, and macrophyte abundance (Dillon et al. 1978; Hendrey et al. 1976). However, other studies have shown trends in phytoplankton production and nutrient concentrations which were not consistent with the

oligotrophication theory (Dillon et al. 1979; Hendry and Brezonik 1984). Although acid deposition has been studied less intensively in the southeastern U.S., some trends in acid deposition and its aquatic effects have been demonstrated for Florida. Brezonik et al. (1980) found that the northern two-thirds of Florida receives a mean annual rainfall pH of 4.7 or less and excess sulfate deposition (non-marine origin, based on SO_4:Cl ratios) around 20 kg/ha·yr. Furthermore, Florida has approximately 2500 lakes that are sensitive to acidification based on the criterion of alkalinity <100 μeq/L (Hendry and Brezonik 1984). In a study of 20 soft-water Florida lakes over the pH range 4.6–6.7, Brezonik et al. (1984) found strong correlations of phytoplankton, chlorophyll-*a*, and total phosphorus with pH. Data from 165 Florida lakes were analyzed by Canfield (1981), who concluded that the relation between pH and chlorophyll-*a* was due to a strong correlation of TP with pH rather than to other factors related to pH. However, his data base included many hard-water and eutrophic lakes, which would tend to mask a pH-TP or pH-chlorophyll-*a* correlation in soft-water lakes.

These survey results have left it unclear whether the low TP concentrations (and thus low chlorophyll-*a* and phytoplankton levels) in acidic lakes are a consequence of low pH (as suggested by Grahn et al. 1974) or whether they reflect the conditions that originally make the lakes susceptible to acidification. Lakes with small watersheds receive a large proportion of their water and phosphorus inputs from rainfall directly to the lake surface. There is thus little opportunity for watershed buffering, and phosphorus loading rates to such lakes are low.

Phosphorus is a major nutrient requirement of primary producers in aquatic and terrestrial habitats. In lakes, phosphorus availability is the factor which most often limits phytoplankton production. Increased cultural input of phosphorus was recognized as the primary cause for the eutrophication of many lakes during the 1960's and 1970's. The key role of phosphorus in the eutrophication process led to much research on ways to control or reduce phosphorus levels in lakes. Although this research necessarily included the processes involved in phosphorus cycling, the primary emphasis was on productive lakes. Some phosphorus cycling studies have considered temperate oligotrophic lakes, but few have included unproductive subtropical lakes.

Lake acidification seems to have the opposite effect of eutrophication, but the role of pH in determining lake productivity remains a controversial issue. As mentioned earlier, lake surveys from different geographic areas have found decreasing TP concentrations as $[H^+]$ increases. On the other hand, although acidic lakes generally tend to be unproductive, some evidence indicates that acid lakes are no less productive than similar, oligotrophic lakes with circumneutral pH values (Dillon et al. 1979).

Objectives

This dissertation addresses the hypothesis that acidification of Florida lakes can directly or indirectly affect their total phosphorus concentrations. The approach taken to answer this question involved a combination of laboratory and field studies designed to accomplish the following major objectives:

1. to characterize phosphorus cycling in an acidic, subtropical lake, and
2. to assess the effect of $[H^+]$ (acidification) on the major processes involved in phosphorus cycling. These include planktonic uptake and turnover of phosphorus, exchange reactions between lake water and sediments, and the release of phosphorus from decomposing organic matter.

Site Description

McCloud Lake is a small, soft-water lake located in the Trail Ridge area of north-central Florida, about 40 Km east of Gainesville in Putnam County (Figure 1-1). Past studies of the lake include its use as a control in a whole-lake nutrient enrichment experiment on nearby Anderson-Cue Lake in 1966–1969 (Brezonik et al. 1969) and quarterly sampling during a 1978–1979 survey of the chemistry and biology of 20 Florida lakes (Hendry and Brezonik 1984). The region is characterized by sparse vegetation and numerous small lake basins perched among sandy hills. Longleaf pine/turkey oak assemblages provide a broken canopy, while lichens and wiregrasses dominate the understory and open areas. The McCloud Lake watershed (1 Km^2) is uninhabitated and is part of a controlled-access area, the University of Florida Katharine Ordway Ecological Preserve.

Surface soils consist of non-spodic marine sands (Candler typic quartzipsamment, cation exchange capacity $\sim$2.5 meq/100 g) that allow very little overland runoff to the lake. Other components of the unconfined (non-artesian) surface aquifer include gravels and sandy

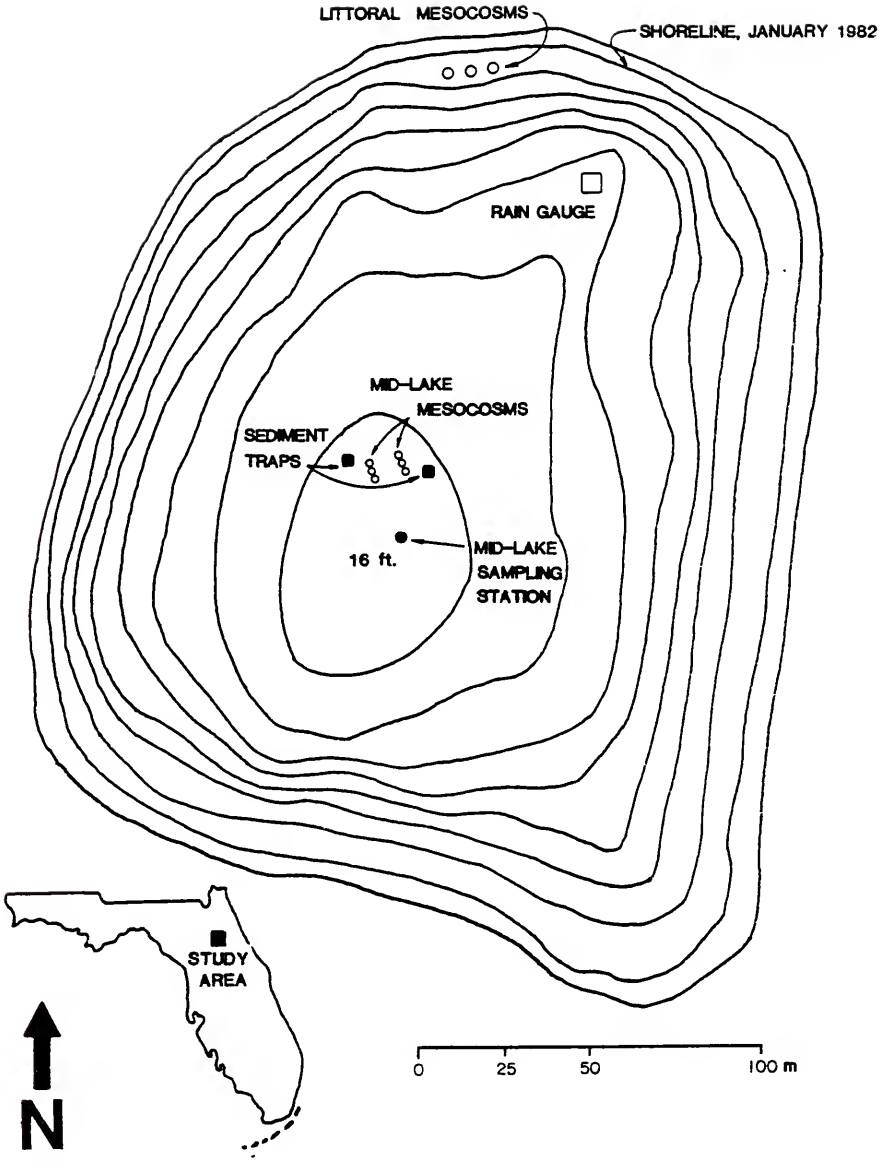

Figure 1-1. Bathymetric map of McCloud Lake, September 1982 (contour interval = 2 ft).

clays of the Citronelle Formation. The sandy clays, clays, and phosphatic sands of the Hawthorne Formation constitute a relatively impermeable confining layer (24–30 m thick) which separates the limestone of the artesian Floridan Aquifer from the perched shallow water table. Since there are no surface inflows or outflows to McCloud Lake, the only sources of water are rainfall directly to the lake and subsurface seepage. The hydraulic residence time of the lake is about 9.6 years (Baker 1984).

McCloud Lake occupies a sub-rectangular solution basin (Figure 1-1) which had a surface area of about 5 ha and a maximum depth of 5 m during 1980–1982. Water level and surface area vary widely in response to long-term rainfall patterns. In 1966–1967, the maximum depth was nearly 6.5 m and the surface area was about 9 ha, while in 1968 the surface area was reduced to 6.8 ha and maximum depth was only 5.5 m (Brezonik et al. 1969).

CHAPTER 2
LITERATURE REVIEW

Phosphorus cycling in aquatic environments is the result of many processes which involve different phosphorus forms and numerous storage compartments, as generalized in Figure 2-1. While inputs and losses determine the total phosphorus concentration in a lake, within the lake soluble inorganic phosphorus is incorporated into organic compounds by primary producers, cycled through dissolved and particulate compartments, and returned to inorganic form. The duration of individual processes can vary from seconds to days or months, and the relative importance of any particular compartment or transformation varies from one lake to another. Because of the importance of phosphorus as a major plant nutrient and its role in lake eutrophication, many researchers have studied the aquatic phosphorus cycle. Their approaches have ranged in scope from focusing on one process or compartment, to complex mathematical models designed to simulate the major processes that control lake phosphorus concentration. The following review considers research in the major areas included in this study.

Sediment-Water Exchanges

Lake sediments act as a net sink for phosphorus through accumulation of particulate organic matter, but under certain conditions they

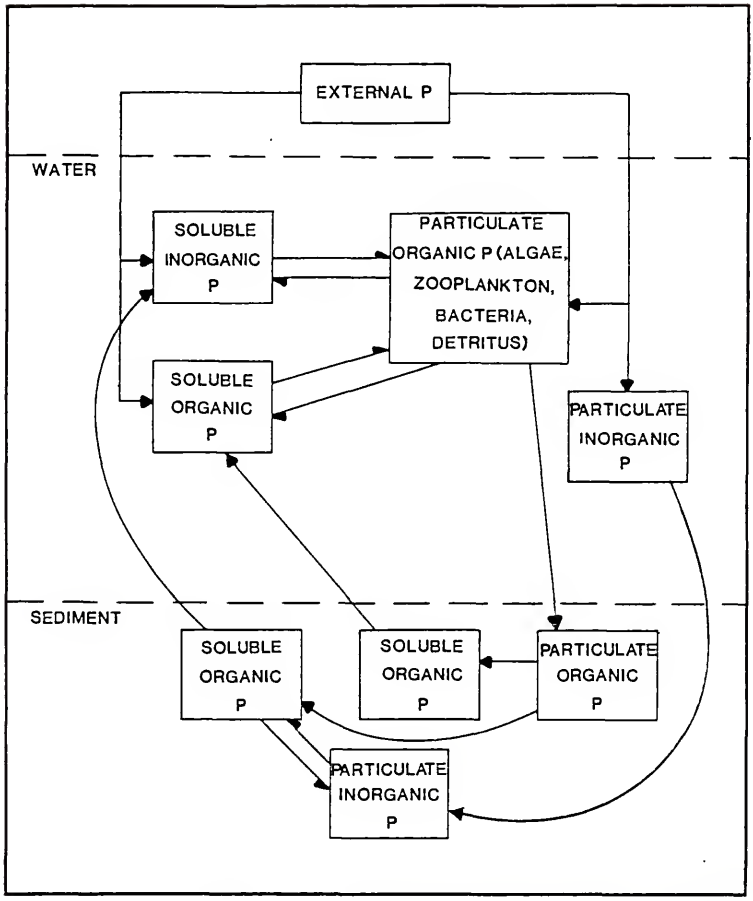

Figure 2-1. Generalized pathways of phosphorus cycling in lakes (after Syers et al. 1973).

can constitute a significant source to lake water. Early studies of the effectiveness and fate of phosphate fertilizers have contributed to our understanding of the behavior of phosphorus in sediments. The realization that a large fraction of phosphorus in fertilizer was fixed or retained in soil led to investigations of the mechanisms involved. Coleman (1944a, 1944b) found that the presence of iron and aluminum oxides was more important for phosphorus fixation than the type of clay in coarse or fine soil fractions, and he suggested that retention involved an exchange of OH^- for $H_2PO_4^-$ at the oxide surface. Other soils researchers corroborated the importance of iron and aluminum oxides in phosphate fixation (Swenson et al. 1949; Haseman et al. 1950) and demonstrated that some organic acids can decrease phosphate retention over specific pH ranges by forming complexes with the Fe and Al (Struthers and Sieling 1950; Bradley and Sieling 1953).

It was unclear whether phosphate retention involved adsorption or precipitation until Fried and Dean (1955) concluded that because a large portion of fixed phosphate was exchangeable with carrier-free inorganic ^{32}P, adsorption must be the principal mechanism. Hingston et al. (1967) demonstrated that retention of phosphate on oxide surfaces is a specific adsorption mechanism which is independent of the properties of the diffuse double layer or the outer Helmholtz layer. Adsorption is accomplished by exchange of the anion for water and hydroxyl ions at the oxide surface, and the reaction always results in a decrease in surface charge. They further pointed out that an undissociated free acid and its most highly charged anion are not adsorbed if present alone because of the requirement for a proton donor and acceptor for specific adsorption to occur. Maximum adsorption of

phosphate increases as pH decreases, with a discontinuity near each pK value, and $H_2PO_4^-$ is the form most readily adsorbed.

Mortimer (1941, 1942) included phosphorus in his studies of mud-water exchanges of dissolved substances. He found that anoxic conditions at the sediment-water interface cause an increased release of phosphate to the water. Numerous other studies have reaffirmed the relation between anoxic bottom water and enhanced release of phosphate from sediments (Porcella et al. 1970; Li et al. 1972; Syers et al. 1973; Kamp-Nielsen 1974; Fillos and Swanson 1975; Armstrong 1979). Reduced forms of iron and manganese are soluble, and mobilization of these elements from lake sediments into anoxic bottom water also solubilizes adsorbed inorganic phosphorus (Mortimer 1971; Syers et al. 1973; Armstrong 1979). Vertical mixing processes can recycle the phosphorus to the euphotic zone, where it would be available for biological uptake. Kamp-Nielson (1974) reported a linear relationship between the release of phosphate and its concentration gradient across an anaerobic mud-water interface, but he found that sorption reactions dominated phosphate exchange under oxygenated conditions. Other workers (Hynes and Grieb 1970; Fillos and Swanson 1975) have reported sediment phosphate release under aerobic conditions, but at a much slower rate.

The amount of sediment inorganic phosphorus available for release to overlying lake water depends on the size of this phosphorus pool and on sediment characteristics. Li et al. (1972) estimated exchangeable inorganic sediment phosphorus by following the rate of disappearance of inorganic carrier-free ^{32}P from solution in well-mixed sediment-water systems. The exchangeable fraction of four Wisconsin lake sediments ranged from 19% to 43% of total inorganic phosphorus for both

aerobic and anoxic conditions, although a significant release of sediment inorganic phosphorus occurred under anoxic conditions. Porcella et al. (1970) set up microcosms with sediments as the only source of phosphorus for algal growth. They observed a repeatable series of events in which phosphorus released to an anaerobic layer above the sediment surface led to a benthic mat of the blue-green alga Oscillatoria sp., followed by a bloom of the same species in the overlying water. The authors concluded that the Oscillatoria mat enhanced sediment phosphorus release by disrupting the sediment-water interface when bubbles occasionally lifted portions of the mat and attached sediment.

Biological reworking of sediments is another mechanism that can accelerate sediment-water phosphorus exchange. Davis et al. (1975) investigated the effect of burrowing tubificid worms on phosphorus dynamics in intact mud-water columns. The worms caused an increased removal of ^{32}P from the water (this became bound to Fe and Al oxides), but did not affect release of ^{32}P back into the water. In subsequent bioturbation studies (Gallepp et al. 1978; Gallepp 1979), burrowing larvae of chironomid midges increased the phosphorus concentration in overlying water, but the increase was attributed to excretion rather than an accelerated sediment release.

Lake sediments can adsorb large amounts of added phosphorus in addition to serving as an internal source of inorganic phosphorus. This ability of sediments to buffer aquatic phosphate concentrations has been pointed out by numerous workers (Carritt and Goodgal 1954; Hayes and Phillips 1958; Phillips 1964; Pomeroy et al. 1965; Harter 1968). Carritt and Goodgal (1954) demonstrated that retention of

inorganic phosphorus by estuarine sediments involves a rapid initial adsorption process followed by a slower diffusion reaction.

The phosphate adsorbed by sediments from a eutrophic Connecticut lake (Harter 1968) was associated with two sediment fractions: a loosely bound iron fraction and a more tightly bound aluminum fraction. The work of Shukla et al. (1971) with sediments from nine soft-water and five hard-water Wisconsin lakes showed that noncalcareous sediments adsorbed more phosphorus than did calcareous sediments. Furthermore, phosphorus adsorption by both sediment types was corelated more closely with oxalate-extractable Fe than with any other parameter. The authors postulated that adsorption occurred on a large complex consisting primarily of hydrated Fe oxide, with smaller amounts of organic matter, Al_2O_3 and $Si(OH)_4$.

Decomposition

The amount of inorganic phosphorus present in sediment interstitial water is affected by sediment characteristics and by decomposition of organic matter. The effect of various environmental parameters on phosphorus release from decomposing algae and aquatic macrophytes has been studied in field and laboratory situations. In a summary of previous studies, Foree et al. (1970) listed three general stages in the nutrient regeneration process: (1) A rapid ($\sim$24 h) initial step in which nutrients are released, absorbed, or released and then reabsorbed; (2) a stationary phase of several days with no net change in nutrient concentration; and (3) active net release of nutrients to solution over several hundred days.

Foree and McCarty (1968) followed phosphorus release during the anoxic decomposition of cultured algae. They found that after 200 days of incubation about 40% of the initial particulate phosphorus remained in refractory solids. In a related study, the same group (Foree et al. 1970) developed a mathematical model to describe phosphorus regeneration under anoxic and aerobic conditions as a function of measurable quantities. However, the applicability of their model is limited by the fact that some of the terms can only be obtained after lengthy laboratory decomposition studies. After one year of decomposition a larger fraction of initial particulate phosphorus remained in the aerobic ($\sim$50%) than in the anoxic ($\sim$40%) experiments.

Nichols and Keeney (1973) followed the release of phosphorus from herbicide-killed aquatic macrophytes (Myriophyllum exalbescens) in water-only and water-plus-sediment systems. They found a rapid initial release of soluble organic phosphorus after the plants were killed, followed by an increase in inorganic phosphorus. Levels of inorganic phosphorus were lower in the systems that contained sediments. The authors concluded that phosphorus released from plants decomposing in a lake was available for incorporation into biomass or adsorption onto sediments.

Acid and alkaline phosphatase enzymes produced by bacteria and algae are important in the remineralization of organic phosphorus compounds. Reichardt (1975) found sharp increases in bacterial biomass and alkaline phosphatase activity in the first 1 cm of lake sediments and noted that below the upper aerobic layer, bacterial densities decreased while enzyme activity remained nearly constant. He concluded

that the phosphatases at this sediment depth were longer-lived than the bacteria that produced them.

Landers (1982) conducted field decomposition studies in the littoral zone of a soft-water Indiana reservoir. He isolated areas with and without naturally senescing Myriophyllum spicatum in open-ended plastic enclosures and observed changes in nutrients and chlorophyll-a over 119 days. Phosphorus released from the macrophytes (extrapolated to a whole-lake basis) equalled about 2–18% of the total annual phosphorus loading to the lake, and concurrent increases in chlorophyll-a indicated a significant phytoplankton response to the release.

Planktonic Phosphorus Cycling

Observations that nearly undetectable levels of dissolved inorganic phosphorus are often adequate to support phytoplankton blooms led to the hypothesis that phosphorus cycling within the water column is a rapid process. The use of radioactive ^{32}P has facilitated accurate estimates of planktonic phosphorus uptake rates and turnover times with addition of as little as 0.002% of ambient inorganic phosphorus levels. Hayes and Phillips (1958) and Phillips (1964) used ^{32}P to study phosphorus equilibrium in systems containing mud, water, plants and bacteria; they summarized their findings and earlier work to provide an integrated concept of phosphous cycling among the components of a whole-lake system. Their estimated turnover times included 1 week for the water of a whole lake; 0.3 days for bacterial or phytoplankton cells (but 5 min for initial equilibration); 3–4 days for rooted aquatic macrophytes; and 1 day for zooplankton (which can utilize only

organic phosphorus). The authors emphasized the influence of bacteria in retaining phosphorus in the water column through incorporation into organic forms (and thus preventing adsorption by sediments) or by accelerating the return of phosphorus from the sediments.

Rigler (1964) examined water column phosphorus fractions in different types of temperate North American lakes and found that soluble organic phosphorus (SOP) represented about 18% of total phosphorus (TP) in all trophic types. He attributed wide variations in SOP reported in the literature to variations in filter pore size and methods used to remove seston from the water. He found that turnover of inorganic phosphorus by seston (using carrier-free ^{32}P) was less than 10 min in all eight lakes during the summer, and increased in winter. Rigler (1966, 1968, 1973) later contended that his ^{32}P uptake data demonstrated that colorimetric analyses overestimate inorganic phosphorus concentrations. However, as pointed out by Lean and White (1983), the inconsistency in Rigler's data was due to his failure to consider that plankton could excrete unlabelled inorganic phosphorus, rather than overestimation.

Understanding of planktonic phosphorus cycling was advanced by Lean (1973a, 1973b), who used Sephadex gel to separate soluble ^{32}P fractions on the basis of molecular size. From his results with this technique in a eutrophic Canadian lake, Lean proposed a generalized description of phosphorus movement between biologically important forms. He demonstrated the rapid formation of a dissolved algal or bacterial organic phosphorus compound (molecular weight about 250) that becomes associated with a high-molecular weight colloid, releasing orthophosphate in the process. The colloidal phosphorus form comprises

a large proportion (about 77%) of nonparticulate phosphorus, but this fraction is not available for algal uptake.

Both chemical and radioisotope methods can be used to study phosphorus uptake by lake plankton. The application of these methods and the significance of their results were recently reviewed by Lean and White (1983), who used both techniques to estimate phosphorus uptake rate constants for the same lake samples. They concluded that small cells dominate uptake when low amounts of phosphorus are added, while at high added phosphorus concentrations, uptake is primarily by large cells. The comparison of phosphorus uptake rates by seston from different lakes is therefore practically impossible because of differences in size distribution of plankton and variations in amounts of phosphorus added by different researchers.

Zooplankton phosphorus excretion has long been recognized as a recycling mechanism in the water column, but there has been little agreement about its relative importance or whether organic or inorganic forms predominate. Johannes (1965) investigated interactions between marine protozoa and bacteria and their effect on phosphorus cycling. He found that protozoan phosphorus excretion (per unit weight) is 1–2 orders of magnitude faster than that of marine microcrustaceans, and several orders of magnitude faster than marine macrofauna. The protozoan-bacterial interaction involves consumption of organic detritus by bacteria, which in turn are grazed by protozoans. Bacterial populations are maintained in a state of "physiological youth" by protozoan grazing, thus increasing regeneration of inorganic phosphorus. Buechler and Dillon (1974) found that phosphorus uptake by freshwater ciliated protozoans (Paramecium spp.) was effected by ingestion of bacterial biomass, and that phosphorus turnover rates were extremely fast.

Hargrave and Geen (1968) measured rates of excretion of unlabelled soluble phosphorus for several species of marine crustaceans and one rotifer. Although soluble organic phosphorus constituted up to 75% of the amount regenerated, they calculated that zooplankton released enough inorganic phosphorus to the photic zone to supply one-fifth to two times the daily phytoplankton requirement. In all cases the measured excretion rate was decreased by increased bacterial activity and experimental duration. Use of Sephadex to fractionate labelled phosphorus compounds has provided an explanation for these observations (Peters and Lean 1973; Peters and Rigler 1973). This technique showed that about 90% of soluble phosphorus released by Daphnia rosea and Diaptomus minutus was inorganic phosphorus. However, bacteria quickly assimilated most of the released inorganic phosphorus, which accounts for the relation Hargrave and Geen (1968) found between phosphorus excretion and bacterial activity or length of incubation. Bacterial uptake also explains the high proportion of SOP found by earlier workers. Peters and Rigler (1973) further estimated that overall phosphorus cycling efficiency of zooplankton [(P regenerated)/(P regenerated + P sedimented) x 1000] is as high as 88–93%, which again emphasizes the important role of zooplankton excretion in maintaining phosphorus in the water column.

As pointed out by Johannes (1965) for marine zooplankton, there is an inverse relationship between body size or body weight and rate of phosphorus regeneration, so that small species are potentially more important in regenerating soluble phosphorus than larger forms. This relationship has been noted by numerous others (e.g., Hargrave and Geen 1968; Peters and Rigler 1973), and it implies that a lake's trophic

state could be affected by processes which change the size distribution of its zooplankton.

Fish constitute another influence on water column phosphorus cycling. Kitchell et al. (1975) employed a mass-balance approach to evaluate the importance of phosphorus flux through fishes. They calculated that production of fish biomass fixes 60–70% of the annual phosphorus input to Lake Wingra, Wisconsin. The fraction that is incorporated into bones and scales (∿50%) will not be remineralized through decomposition, and thus is effectively lost to the system. However, the authors suggest that the seasonal pattern of fish mortality in temperate lakes (high mortality after spring spawning) results in a significant supply of phosphorus from decomposing fish biomass in late spring and early summer.

Lake Phosphorus Models

Efforts to model phosphorus dynamics in lakes have shown varying degrees of success, depending in part on the complexity and objectives of the modeling efforts. Lake management applications began with a simple mass balance approach to lake phosphorus concentration. This involves estimating the change in lake phosphorus storage that results from a balance of loading terms and loss terms. Non-point sources are usually estimated from land use data, while sedimentation rates frequently are derived from the literature and adjusted to calibrate the model.

By examining the relationship between phosphorus loading and trophic state indicators (e.g., total phosphorus, chlorophyll-*a*, Secchi depth, hypolimnetic oxygen deficiency), Vollenweider (1975), Dillon and Rigler (1974) and others have developed critical loading limits, below

which eutrophication could be avoided. Furthermore, these relationships could be used to predict the effect of changes in loading rates on lake phosphorus concentration, including the time required to reach a new equilibrium after a change in input. The application of some of these models has resulted in the need to modify them to fit observed conditions. Yeasted and Morel (1978) used a combination of phosphorus budget modeling and stepwise discriminant analysis to evaluate the ability of water residence time, mean depth, and lake surface area to describe the non-conservative behavior of phosphorus in 128 phosphorus-limited lakes (71 eutrophic, 42 mesotrophic, and 15 oligotrophic). They found that only hydraulic residence time gave consistent statistical significance. Shannon and Brezonik (1972) and Baker et al. (1981) have developed nutrient loading-trophic state relationships specific to Florida lakes.

In spite of the problems inherent in the application of mass balance models, their very simplicity makes them an attractive management tool. They can be used with a reasonable degree of accuracy to simulate and evaluate the effect of various options, provided data are collected carefully and the assumptions are not violated.

In contrast to the simple mass balance approach are more complex approximations of the non-conservative behavior of phosphorus within a lake. These models use differential equations to represent changes in various processes (e.g., production of phytoplankton biomass) as a function of time. Models involving phosphorus range from those that consider only phytoplankton as a biotic component (Fleming 1975) to more complex, multi-component ecosystem models (Chen 1969). The simpler models do not yield realistic results, but it is difficult to obtain all the coefficients needed in more complicated models.

Nevertheless, ecosystem modeling provides the only feasible alternative for integrating so many processes and parameters.

Effects of pH on Phosphorus Cycling

Acid deposition and the acidification of surface waters are recent enough phenomena that most research has been focused on identifying effects and documenting the extent of affected areas, instead of identifying the mechanisms involved. As mentioned earlier, while many studies have shown decreasing TP levels with decreasing lake pH, there is little evidence to link the observed TP decrease to acidification. Most available information concerning pH effects on phosphorus dynamics relates to sediment-water interactions and decomposition.

MacPherson et al. (1958) examined the effect of pH on the partitioning of inorganic phosphorus between water and the mud of unproductive, moderately productive, productive, and acid bog lakes. They found similar trends in all lake types, with minimum phosphorus release from the mud in the pH range 5.5—6.5. More inorganic phosphorus was released at higher and lower pH values. The acid bog and productive lake muds did not adsorb appreciable amounts of added phosphorus; the unproductive lake mud removed most of the added phosphorus in the acid pH range but not at pH 7. Increased phosphorus adsorption as pH decreases has been shown for soils (Lopez-Hernandez and Burnham 1974). Andersson et al. (1978) and Gahnstrom et al. (1980) varied the pH of water overlying sediment cores from acidic and alkaline Swedish lakes. They found more inorganic phosphorus was released from the sediments at high pH than at low pH.

Consideration of the effect of pH on solubility of metal phosphates shows the controlling phases under equilibrium conditions (Stumm and Morgan 1981). At low pH strengite ($FePO_4$) and variscite ($AlPO_4$) are the solid phases that may control phosphate solubility, while above pH 6 calcium phosphates (notably apatite) are the predominant solids. However, due to rapid biological transformations, equilibrium is rarely attained in the pH range of natural waters.

Singer et al. (1983) added ^{32}P to the water over intact sediment cores from an acidic Adirondack lake. Some had a mat of Sphagnum sp., and two concentrations of aluminum were used (0 and 300 µg/L). They concluded that the algal mat was much more efficient than bare sediment at removing water column phosphorus, and that precipitation reactions (with Al concentrations up to 300 µg/L) were unimportant.

Grahn et al. (1974) theorized that acidification inhibits decomposition because of the accumulation of organic matter which they observed in the sediments of many acid lakes. Studies on the effect of pH on decomposition have been inconclusive. Some measures of decomposition, such as leaf litter weight loss and numbers of total bacteria, decrease at low experimental pH (Leivestad et al. 1976; Traaen 1980). Others (sediment oxygen demand, glucose turnover) show no effect of reduced experimental pH (Andersson et al. 1978; Gahnstrom et al. 1980), although sediment oxygen demand and glucose turnover both increased in lakes after lime treatment. Finally, the experimental acidification of a Canadian lake (Schindler 1980) resulted in no significant change in TP and no evidence of decreased decomposition over 3 years. However,

it should be pointed out that the pH change during this period was only from 6.6 to 5.6.

Another potential effect of lake acidification relates to the importance of pH in controlling phosphate uptake by algae (Wetzel 1983). Different species have distinct pH ranges in which they show optimum growth and phosphate uptake. This is due in part to the pH specificity of extracellular or membrane-associated enzymes, but pH can also alter the permeability of the cell membrane and change the ionic form of inorganic phosphate in the growth medium.

CHAPTER 3
PHOSPHORUS DYNAMICS IN MCCLOUD LAKE

This chapter includes a discussion of the general limnology of McCloud Lake as well as the contributions of important processes and storage compartments to the dynamics of phosphorus cycling within the lake. The historical data base for McCloud Lake is examined, as well as the results of laboratory and *in situ* experiments.

Materials and Methods

Routine Sampling

Limnological data were collected monthly at a mid-lake station from October 1980 through September 1982. Field data included Secchi disk transparency, and temperature and dissolved oxygen profiles, which were measured with a YSI model 54A DO meter. In the laboratory specific conductance was measured with a YSI model 31 conductivity bridge; pH was measured with a Fisher Accumet model 230A pH/ion meter equipped with an Orion internal reference calomel electrode. Chemical samples were collected at 1.0-m intervals and stored in separate polyethylene bottles for major ions (conc. HNO_3 to pH < 2) and nutrients (1 mL saturated $HgCl_2$ per L of sample). Chlorophyll-*a* and phytoplankton samples were collected as a water column composite (1-m intervals), while zooplankton were collected by vertical tows of a #20 Wisconsin plankton net (80 μm mesh). Phytoplankton and zooplankton

were preserved with 1% Lugol's iodine and 5% buffered formalin, respectively.

Standard procedures were followed for all chemical analyses (APHA 1980; U.S. EPA 1979). Major cations were analyzed (flame mode) on a Perkin-Elmer Model 5000 atomic absorption spectrophotometer. Chloride, sulfate, silica, and nutrient forms were analyzed by automated colorimetric procedures (Table 3-1). Semi-micro digestion procedures were used for total phosphorus (autoclaved persulfate digestion) and total Kjeldahl nitrogen (block digestion).

Chlorophyll-a was measured by the trichromatic method (APHA 1980). Phytoplankton aliquots (10–30 mL) were concentrated in Utermohl chambers and counted using methods described by Lund et al. (1958). Zooplankton were identified and counted in 1-mL Sedgwick-Rafter cells under a light microscope.

Phosphorus Budget

Water budget. Monthly data for precipitation, seepage, evaporation, and change in McCloud Lake level (stage) were compiled by Baker (1984), who also discussed the equipment and methods used to collect the data. The resultant water budget is a necessary prerequisite for the construction of a phosphorus budget for the lake.

Stage-area and stage-volume relationships were determined from a bathymetric map of McCloud Lake (Figure 1-1). I constructed the map from 14 fathometer transects and aerial photographs taken in January 1982, which corresponded to the lowest lake stage during the 1980-1982 period. Nine north-south and five east-west transects were run using a Lowrance model 1510B Truline recording fathometer in a skiff powered by

Table 3-1. Automated colorimetric procedures used in McCloud Lake study.

Parameter	EPA Method
Chloride	325.1
Sulfate	375.2
Silica	370.1
Ammonium	350.1
Nitrate + Nitrite	353.1
Phosphorus	365.2

a small outboard motor at constant speed. The ends of the tranects were marked with black plastic sheeting and white plastic milk bottles to ensure their visibility in the subsequent aerial photography. In addition, the distances from markers to the beginning or end of each fathometer transect were recorded.

An outline of the lake (including the transect markers) was drawn from the best aerial photograph, and the scale was determined from measured distances between markers. Changes in depth along each transect were plotted on this outline map, and contours were drawn at 2-foot depth intervals. Lake stage was 2 feet higher on September 22, 1982, than when the bathymetric survey and aerial photography were conducted. This new shoreline was added to the bathymetric map from measurements of distances between the transect markers (which were still marked by wooden stakes) and the new lake shore.

The volume and area of the lake were calculated for each date with a Hewlett Packard 9810A calculator equipped with a digitizer surface. These data were used to establish the stage-area and stage-volume relationships needed for the water budget calculations.

Atmospheric phosphorus loading. Rainfall samples collected at the lake from September 1981 to August 1982 were analyzed for TP. Total phosphorus deposition rates (wetfall and dryfall) were estimated from the relation between wet and total phosphorus deposition measured at several sites in Florida (Brezonik et al. 1983).

Sedimentation. Rates of sedimentation of particulate matter and phosphorus were measured in McCloud Lake with cylindrical sediment traps (Figure 3-1). Design of the traps followed the general recommendations of Blomqvist and Hakanson (1981), who published an extensive

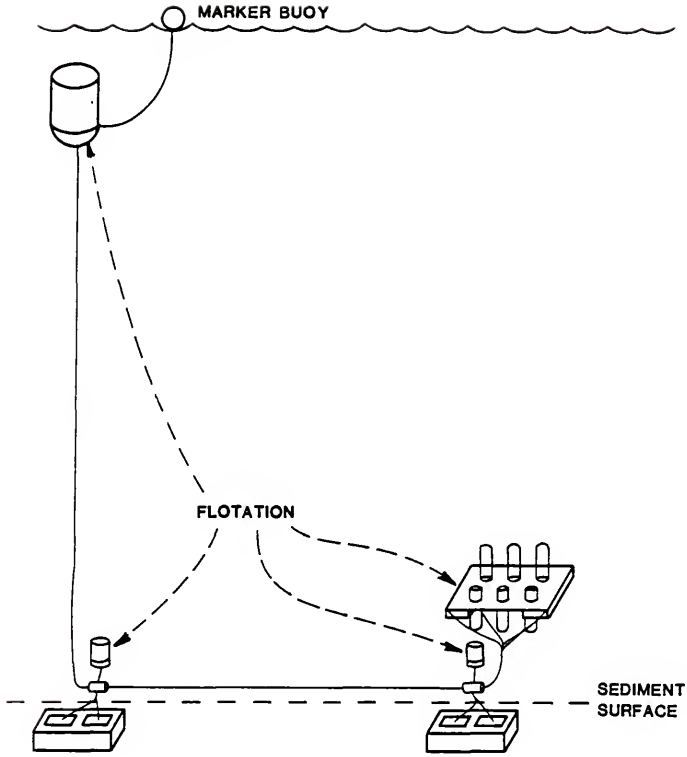

Figure 3-1. Sediment trap design.

review of the design and performance of sediment traps in aquatic systems. They concluded that a simple cylinder gives better results than other shapes when a proper height-to-diameter ratio (H/D) is used to limit resuspension losses. In general they recommended a vessel with diameter $\geq$ 20 mm and H/D $\geq$ 3 or 4.

The base of the traps consisted of a plexiglass rectangle (20 x 27 cm) with six holes for the cylinders and plastic foam for flotation. Rubber bands around the Pyrex test tubes (22 x 150 mm, H/D = 6.7) prevented them from falling through the holes. This buoyant trap apparatus was moored $\sim$0.4 m above the lake bottom in the center of the lake ($\sim$4.5 m total depth). Removal of the large flotation bucket allowed the trap platform to float up to the surface to facilitate recovery of the test tubes with minimal disturbance of the sediments.

Three of the six tubes were placed upright to trap sedimenting particulate matter, while the other three were installed upside-down to estimate the biomass of colonizing invertebrates and attached algae. At the beginning of the first incubation period the platform was raised to the surface and six tubes were installed. The platform was then carefully lowered from the surface using the mooring line, and the flotation bucket was attached approximately 0.5 m below the lake surface to maintain a constant tension.

At the end of each incubation period (30 or 60 days), I carefully swam down to the trap array and inserted rubber stoppers in all six tubes. The bucket was removed from the mooring line so the platform could be raised to the the surface for recovery of the tubes. After new tubes were installed the platform was again carefully lowered to initiate a new incubation.

The test tubes were tared in the laboratory prior to incubation. After an incubation, the outsides of the stoppered tubes were carefully cleaned to remove any attached particulates. The stoppers were removed and the tubes were placed in a drying oven (~60°C) to evaporate all water. When the contents were dry, each tube was cooled and reweighed to allow calculation of sedimentation rates on a dry-weight basis. Next, 20 mL of distilled deionized water was added to each tube and a wet persulfate digestion was performed in the autoclave. Total phosphorus was measured as SRP in the filtered digestate.

McCloud Lake Phosphorus Compartments

In addition to the water column phosphorus analyses previously described, two other in-lake reservoirs of phosphorus were evaluated.

Macrophyte survey. At the beginning of this study in December 1980, McCloud Lake sediments were relatively barren and free of algae or higher plants except in the very shallow littoral areas, where some emergent species were found. However, during the study two submersed macrophytes, Websteria ap. and Eleocharis sp., became established in significant proportions in both littoral and deeper areas of the lake. In September 1982, a survey was conducted to determine the areal extent and density of these macrophytes and to estimate the amount of phosphorus bound in their biomass.

I sampled 14 transects spaced around the lake by swimming (with SCUBA equipment) from the shore out toward the lake center. Each transect started at a marker used in the bathymetric survey in order to facilitate mapping the macrophytes. Data recorded for each transect included the distances from shore and depths at which the macrophytes

beds began and ended, as well as the dominant species. In addition, a composite macrophyte sample was obtained for each transect by manually collecting all plants within a quadrat (0.016 m^2) which was randomly placed at four points more or less evenly spaced along the transect. Additional samples of Eleocharis and Websteria were collected for digestion and TP analysis.

The composite samples were carefully washed in the laboratory and dried in tared envelopes at 60°C to get dry weight per unit area. Subsamples (0.5 g) of dried tissue were ashed at 500°C and ash-free dry weight was calculated. The samples collected for phosphorus analysis were also washed and dried at 60°C. Weighed subsamples ($\sim$0.1 g) were placed in large test tubes; distilled deionized water (20 mL) was added and a wet persulfate digestion was performed in the autoclave. Total phosphorus was measured by the SRP procedure on an aliquot of the filtered digestate.

Sediment phosphorus. A composite surficial sediment sample was collected from the center of McCloud Lake by pooling 6 grabs of a petite Ponar dredge. Subsamples of this sediment were analyzed for TP using a method which involved ashing at 550°C followed by HCl digestion, as described by Andersen (1976).

Phosphorus uptake. Rates of phosphorus uptake and turnover were measured for the submergent macrophytes and for mid-lake seston using radiolabeled (^{32}P) orthophosphate. Intact Eleocharis plants were collected from the lake, transferred to the lab, and carefully washed to remove sediment and attached algae. The washed plants were blotted dry and about 2.0 g of intact plants were placed in each of four PVC trays in 250 mL of membrane-filtered (0.45 μm) lake water at room

temperature. Two trays were covered with aluminum foil to exclude light, and the other two plus a control (250 mL filtered lake water without plants) were incubated under fluorescent light.

An aliquot (1 mL) of a stock solution of ^{32}P enriched orthophosphate solution was added to each tray, and its disappearance from the medium was followed by periodically withdrawing 1-mL aliquots. These samples were placed in scintillation vials and counted with a liquid scintillation counter.

Mid-lake seston samples (1 L) were incubated under fluorescent light and slowly mixed with magnetic stirrers. Aliquots of a stock K_2HPO_4 carrier for $^{32}PO_4$ were added to the seston samples, and uptake of ^{32}P was followed by periodically withdrawing and filtering 5-mL subsamples through 0.45 μm membrane filters. Methods used to analyze ^{32}P samples and to plot and analyze the data are discussed in Chapter 4.

Results and Discussion

Limnology and Historical Nutrient Trends

McCloud Lake has uncolored, soft water that usually is clear. Conductivity is low (~40 μmho/cm), and divalent cation (Ca^{+2} + Mg^{+2}) concentrations are only about 150 μeq/L. A Secchi disk is visible on the lake bottom during winter months, but Secchi transparency is as low as 1.75 m during summer peaks of phytoplankton. Water clarity is occasionally reduced when littoral sediments are suspended by wave action, but the surrounding hills and small fetch minimize wind influence on the lake.

The water column does not stratify, although bottom temperatures and dissolved oxygen concentrations are generally somewhat lower than surface values (Figure 3-2). The average difference between surface and bottom temperature is 1°C; maximum differences up to 3°C occur during warm months. Percent oxygen saturation shows no difference between surface and bottom waters in winter months, but oxygen saturation is consistently lower near the bottom during warm months, reflecting increased biological activity. Overall, oxygen saturation ranges from 73% to just over 100%, and surface and bottom averages are 93% and 89%, respectively. The generally undersaturated conditions reflect the oligotrophic status of the lake.

The pH of McCloud Lake decreased from 4.85 in 1967–1968 (Brezonik et al. 1969) to 4.71 in 1978–1979, and generally was less than 4.60 during 1980–1982 (Table 3-1 and Figure 3-2). This represents nearly a doubling of H^+ concentration in 15 years. Present pH values correspond closely to rainfall pH. The increase in conductivity from 1967–1968 (32 μmho/cm) to 1980–1982 (42 μmho/cm) indicates that concentration of ions by evaporation may account for some of the pH decline. This hypothesis is supported by the decrease in pH from September 1981 through January 1982 (Figure 3-2) which corresponded to the lowest lake level in 2 years. Lake level began to rise as normal rains resumed in February 1982, and the subsequent pH increase reflected this dilution.

Table 3-1 summarizes nutrient conditions in the lake during 1967–1968 (Brezonik et al. 1969), 1978–1979 (unpublished data), and for the 2 years of this study. There has been remarkably little difference in average nutrient concentrations over this 15-year period. Mean values of several nutrient parameters (TON, TP, SiO_2, TN/TP) for 1978–1979

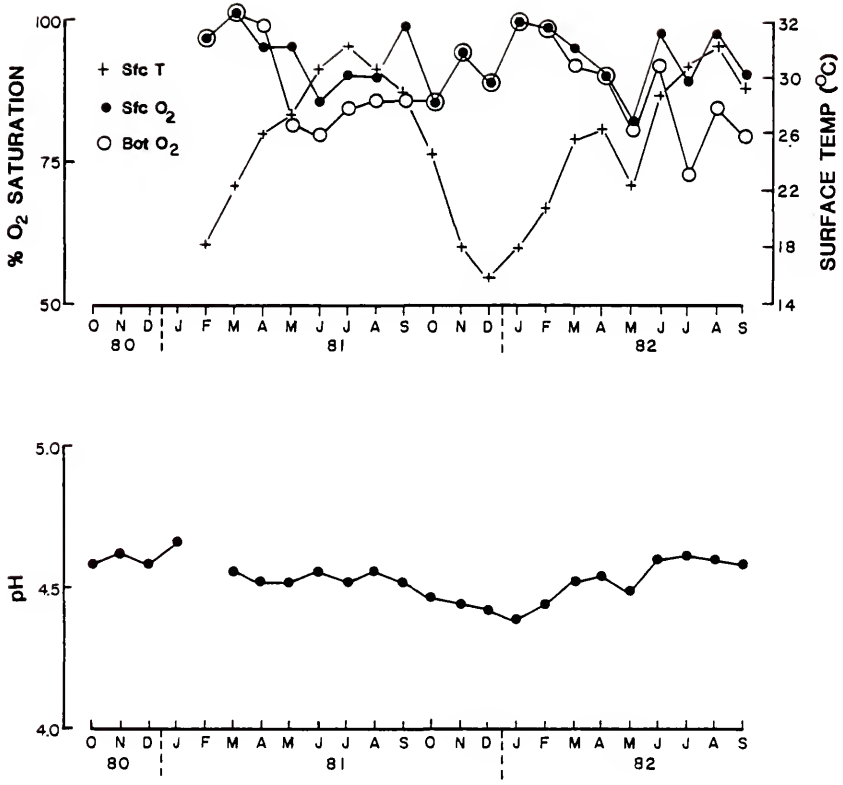

Figure 3-2. Dissolved oxygen and pH trends in McCloud Lake, October 1980 through September 1982.

Table 3-2. Annual means and standard deviations (n = number of sampling dates) of nutrient and limnological parameters for McCloud Lake.

Parameter	1967-68 (n = 12)	1978-79 (n = 4)	1980-81 (n = 12)	1981-82 (n = 12)
pH	4.85	4.71	4.56	4.50
Conductivity*	32	44.8		42 ± 2.6
TON†	420	243	290 ± 120	423 ± 220
NH_4-N†	105	137	62 ± 50	56 ± 40
NO_3-N†	41	47	49 ± 20	68 ± 40
NO_2-N†	1	2	1 ± 0.4	1 ± 1
TP†	12	16	9 ± 3	12 ± 7
SRP†	6	4	5 ± 0.2	3 ± 3
SiO_2†	100	265	213 ± 110	118 ± 70
Chlorophyll-*a*†	1.94	0.88	5.7 ± 2.9	4.7 ± 3.9
TN/TP§	47.3	26.8	44.7	45.7
$\sum$ Ca + Mg**	77	98	147	
SO_4^{-2}**	104	142	140	
$\sum$ Cations**	205	234	313	
$\sum$ Anions**	271	287	310	

*µmho/cm.
†µg/L.
§wt/wt.
**µeq/L.

are not consistent with mean data from the other years, but this may reflect the limited number of sampling dates in 1978–1979 rather than changes in lake chemistry. TON, TP, and NH_4^+-N were lower for 1980–1981 than for 1967–1968. Ammonium in 1980–1982 was about 50% of 1967–1968 levels, but both were low; TON and TP means were identical for the two periods. TN/TP ratios also show little change over the 15 years since 1967–1968, with the exception of the 1978–1979 data. According to criteria proposed for Florida lakes (Huber et al. 1982), the TN/TP value of about 45 (weight basis) indicates that phosphorus is the limiting nutrient in McCloud Lake.

The average chlorophyll-*a* (Table 3-1) during 1980–1982 (5.2 µg/L) was more than two times as high as the mean value reported for 1967–1968 (1.9 µg/L), and was nearly six times the 1978–1979 mean. Nevertheless, these chlorophyll-*a* levels all are indicative of oligotrophic conditions and the differences appear insignificant. A relationship established for TP and chlorophyll-*a* in phosphorus-limited Florida lakes (Huber et al. 1982) predicts that McCloud Lake (TP ≃ 11 µg/L) should have a mean chlorophyll-*a* concentration of 3.1 µg/L. This value agrees well with measured chlorophyll-*a* and indicates that conditions in McCloud are typical of those in phosphorus-limited oligotrophic Florida lakes.

Figures 3-3 and 3-4 show monthly variations in McCloud nutrient and biological parameters from October 1980 to September 1982. TP and TON exhibited maximum values in spring and summer when chlorophyll-*a* and total zooplankton abundances were highest. No trends can be discerned in variations of SRP. Both TP and SRP showed summer increases during 1967–1969. Total phosphorus and TON were generally higher

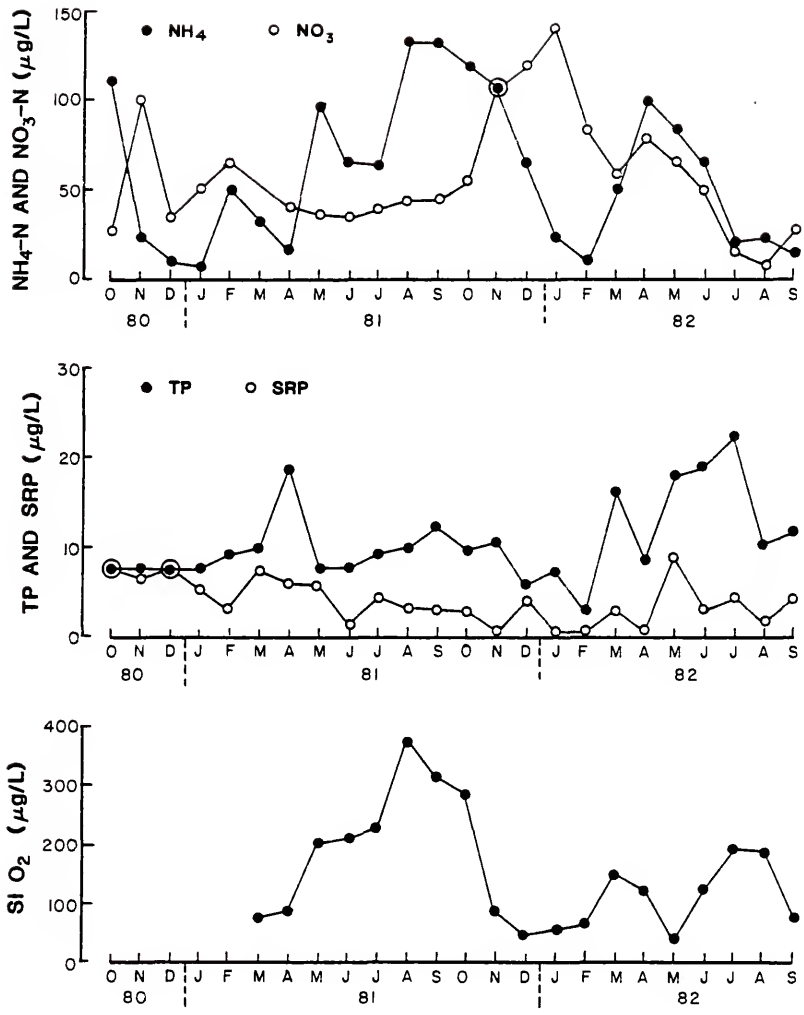

Figure 3-3. Variations in dissolved silica and nitrogen and phosphorus forms in McCloud Lake, October 1980 through September 1982.

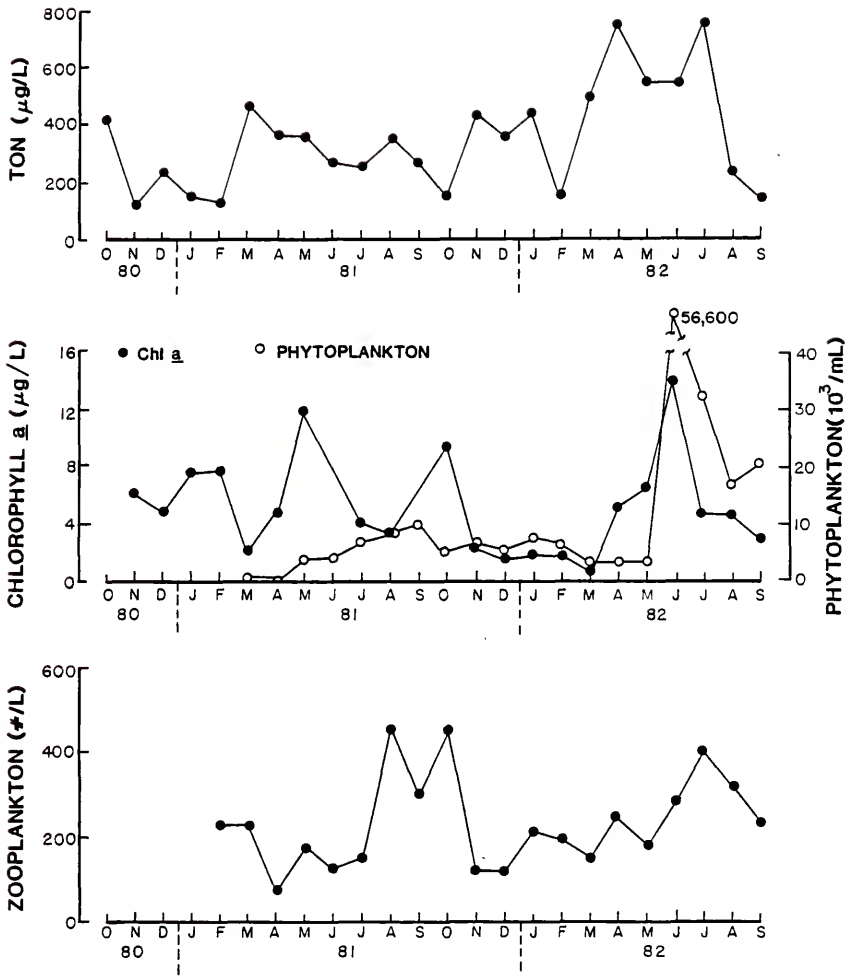

Figure 3-4. Variations in TON and biological parameters in McCloud Lake, October 1980 through September 1982.

throughout the 1981–1982 period than for 1980–1981. The lower TP and TON of 1980–1981 correspond to a drought and falling lake levels, while the higher TP and TON of 1981–1982 reflect increased nutrient loadings due to increased rainfall and rising lake levels.

Nitrate maxima occurred during winter months when biological activity was lowest, and minimum nitrate concentrations corresponded to peaks of phytoplankton and zooplankton abundance. Ammonium showed peaks during warm months and low levels in winter. The sum of ammonium and nitrate was almost never <50 µg/L; maxima of both species were always <150 µg/L, and usually were <100 µg/L. The increase in nitrate and concurrent decrease in ammonium which occured during winter 1981–1982 suggest that nitrification was occurring. Silica concentrations also were low in winter and peaked in mid- to late summer, but never reached levels (>0.5 ppm) considered optimal for diatom production (Fogg 1975; Wetzel 1983).

Chlorophyll-a (Figure 3-4) showed peaks of algal production during spring and fall in 1981 and early summer in 1982, although these trends did not correspond closely to changes in phytoplankton abundance (Figure 3-4). This was probably due to wide fluctuation in densities of microflagellates and small green coccoid and spindle-shape phytoplankters. As a group ultraplankton (1–10 µm) represented an important fraction of total phytoplankton numbers in the lake during both years of the study. A large pulse in ultraplankton occurred during June through September 1982, when total phytoplankton densities exceeded 50,000 cells/mL. With the exception of occasional pulses of Dinobryon cylindricum, D. divergens, and to a lesser extent Asterionella sp., net plankton (>50 µm) rarely constituted a major component of the phyto-

plankton. Oocystis gloeocystiformis consistently formed a large fraction of total phytoplankton and often comprised greater than 50% of total abundance. Other less abundant but common genera included Peridinium, Kirchneriella, Staurastrum, Mallamonas, Cosmarium, and several unidentified penate diatoms. McCloud Lake exhibits an impoverished phytoplankton community with few consistent seasonal trends in species succession. Large masses of filamentous algae were observed in certain areas of the littoral zone in early spring.

Peaks in total zooplankton abundance generally followed peaks in chlorophyll-a. Maximum densities occurred during late summer and fall 1981 and mid-summer 1982 (Figure 3-4). Diaptomus mississippiensis, Eubosmina tubicen, Diaphanosoma sp., and Keratella gracilenta usually comprised 75–100% of total zooplankton numbers. No consistent pattern of species succession was demonstrated, although D. mississippiensis generally increased in importance during summer, while K. gracilenta frequently dominated during winter months. Eubosmina constituted 40–50% of zooplankton totals during September and October 1981 and was a principal sub-dominant in nearly every lake sample. The 34 zooplankton species observed during 1980–1982 included four copepod, five cladoceran, and 25 rotifer species. Except for a reduced standing stock, the zooplankton community of McCloud Lake closely resembles those found in more productive Florida lakes of higher pH.

McCloud Lake Hydrology

Table 3-2 presents monthly precipitation amounts measured at McCloud Lake from August 1981 through July 1982, as well as estimates

Table 3-3. McCloud Lake hydrology data, August 1981 through July 1982.

Date	Precipitation, cm	Lake Volume, 10^3 m^3	Lake Area, 10^3 m^2
1981			
Aug	14.30	134.81	51.57
Sep	7.70	131.09	50.84
Oct	1.58	124.59	49.55
Nov	6.86	123.19	49.27
Dec	4.12	120.56	48.75
1982			
Jan	17.60	121.49	48.94
Feb	9.16	121.33	48.91
Mar	12.50	117.46	48.14
Apr	23.11	130.16	50.65
May	8.47	134.03	51.42
Jun	34.34	134.50	51.51
Jul	13.36	143.17	53.23
TOTAL	153.10		
MEAN		128.03	50.23

of lake volume and surface area calculated from lake stage measurements. Sixty percent of the total annual rainfall occurred between March and July 1982. The dry conditions between August 1981 and February 1982 caused lake volume to decrease by nearly 13% while surface area decreased about 6.5%.

Baker (1984) constructed a water budget for McCloud Lake for the time of this study. He found that precipitation accounted for 90% of the total annual water input, and seepage into the lake contributed the remaining 10%. The sandy soils in the watershed preclude significant surface runoff and allow most rainfall to percolate directly to the shallow water table rather than to the lake. Evaporation was the most important mechanism for loss of water from McCloud Lake during the study, although outseepage rates can exceed evaporation rates when the shallow water table is low.

McCloud Lake Phosphorus Budget

Precipitation. Table 3-3 presents monthly phosphorus deposition to McCloud Lake from August 1981 through July 1982. Wet deposition values are based on TP concentrations in precipitation samples and rainfall amounts. Total deposition rates were estimated from a previous study because dryfall samples were not collected at McCloud Lake. Brezonik et al. (1983) monitored precipitation chemistry with a network of 26 stations in Florida that included four wet-dry collectors (1 urban, 1 coastal, and 2 agricultural stations). Wet TP deposition averaged 20% of total TP (wet plus dry) deposition at the four sites for May 1978 through April 1979. However, dry deposition of phosphorus was more important at the agricultural sites because of fertilizer use

Table 3-4. McCloud Lake phosphorus storage and atmospheric loadings, August 1981 to July 1982.

Month	TP Storage, Kg	Phosphorus			
		Wet, mg/m^2	Wet, g	Total 1,[a] g	Total 2,[a] g
1981					
Aug	1.35	0.810	41.77	126.6	167.1
Sep	1.57	0.405	20.59	62.4	82.4
Oct	1.25	0.126	6.24	18.9	25.0
Nov	1.36	0.755	37.20	112.7	148.8
Dec	0.60	0.376	18.33	55.5	73.3
1982					
Jan	0.85	1.507	73.75	223.5	295.0
Feb	0.36	0.980	47.93	145.2	191.7
Mar	1.88	0.800	38.51	116.7	154.0
Apr	1.04	3.175	160.81	487.3	643.2
May	2.41	0.677	34.81	105.5	139.2
Jun	2.56	3.323	171.17	518.7	684.7
Jul	3.29	1.440	76.64	232.2	306.6
TOTAL		14.374	727.76	2205.2	2911.0
MEAN	1.54				

[a]Assumes Wet = 0.33 total.
[b]Assumes Wet = 0.25 total.

and increased dust associated with agricultural practices. Since McCloud Lake is not located in an area of intense agriculture, two estimates of total TP deposition were calculated, based on assumptions that wet deposition represented 25% and 33% of total TP deposition.

The estimated total TP loading to McCloud Lake ranged from 2.21 to 2.91 Kg/yr, or 43.9 to 58.0 $mg/m^2 \cdot yr$. This range compares favorably with the mean statewide total TP deposition of 51.0 Kg/ha·yr reported by Brezonik et al. (1983), but it is more than double the value they found at rural non-agricultural sites (27.0 $mg/m^2 \cdot yr$). Local land use patterns and annual climatic variations can strongly affect nutrient deposition rates, and it is possible that McCloud Lake is atypical of the rural non-agricultural sites monitored by Brezonik et al. (1983).

Baker (1984) compared atmospheric nutrient deposition rates at McCloud Lake to nutrient loading criteria established by Vollenweider (1968, 1975) and Shannon and Brezonik (1972). He concluded that atmospheric nitrogen loading exceeded the minimum input required to sustain mesotrophic conditions, and that atmospheric phosphorus loading was less than half the minimum mesotrophic loading rate. However, his estimate of phosphorus deposition was based on the average rate at rural, non-agricultural sites from Brezonik et al. (1983). When atmospheric phosphorus loading is estimated from precipitation samples collected at McCloud Lake, two of the three minimum mesotrophic loading criteria are exceeded (Table 3-4). Given the oligotrophic status of McCloud Lake, this suggests that lake acidification may in fact contribute to the low TP and production which are typical of acidic

Table 3-5. Atmospheric deposition of phosphorus at McCloud Lake and loading criteria.

Reference	Units	Minimum* Mesotrophic Loading	McCloud† Total Deposition
Vollenweider (1968)	$mg/m^2 \cdot yr$	44.0	43.9-58.0
Shannon and Brezonik (1972)	$mg/m^3 \cdot yr$	22.0	17.3-22.8
Vollenweider (1975)	$mg/m^2 \cdot yr$	100.0-110.0	43.9-58.0

*Calculated by Baker (1984).
†This study.

lakes. However, more detailed studies using data for many lakes would be necessary to provide a satisfactory answer to this question.

Mass balance. The seepage contribution to total phosphorus loading to McCloud Lake was not evaluated in this study because water in the seepage meters became anoxic, thereby promoting solubilization of TP from the sediments. However, since seepage accounted for only 10% of the annual water input, it was assumed that the relative importance of phosphorus input by seepage was minor. This is supported by the fact that SRP tends to be low in groundwater because it adsorbs to clays and hydrous oxide surfaces. The budget summarized in Table 3-5 indicates that phosphorus has a very short residence time in McCloud Lake (0.5—0.7 yr), which is in keeping with rapid SRP uptake rates and internal phosphorus cycling mechanisms.

Sedimentation

Sediment traps were deployed in McCloud Lake for one 2-month and three 1-month incubations. Gross monthly sedimentation rates were calculated for total dry sediment and for total phosphorus (Table 3-6). Particulate and phosphorus sedimentation rates were higher during summer months when lake productivity was at a maximum. Extrapolation from the 158 days of measured sedimentation to annual figures yields a dry sedimentation rate of 429 $g/m^2 \cdot yr$ and a phosphorus sedimentation rate of 370 $mg/m^2 \cdot yr$. These results are probably overestimates for the lake as a whole since more sediment accumlates in the center of the lake than in littoral areas, but several lines of evidence indicate that the trap estimates are reasonable for the pelagic zone. First, ^{210}Pb dating of one profundal McCloud sediment core indicates that

Table 3-6. McCloud Lake phosphorus budget, August 1981 through July 1982.

Precipitation	
Wet (Kg P)	0.73
Dry (Kg P)	1.48-2.19
Total (Kg P)	2.21-2.92
Mean Storage (Kg P)	1.54
ΔS (Kg P)	1.94
Residence Time (Yr)	0.5-0.7

Table 3-7. Sediment trap results from McCloud Lake (mean ± standard deviation).

Dates	Dry Sedimentation, $g/m^2 \cdot mo$	TP, mg P·g dry wt	Phosphorus Sedimentation, $mg/m^2 \cdot mo$
10/23-12/21/82	25.9 ± 0.78	1.024 ± 0.064	26.5 ± 0.78
04/28-06/03/83	11.8 ± 4.98	0.844 ± 0.084	10.0 ± 4.20
06/03-07/05/83	54.6 ± 1.07	0.802 ± 0.095	43.8 ± 0.86
07/05-08/04/83	66.5 ± 0.54	0.724 ± 0.131	48.2 ± 0.39
MEAN	36.9 ± 22.7	0.849 ± 0.127	31.0 ± 15.3
ANNUAL RATE	429*		378.8†

*$g/m^2 \cdot yr$.
†$mg/m^2 \cdot yr$.

the recent annual sediment accumulation rate is about 300 g dry wt/$m^2 \cdot yr$ (personal communication, Michael Binford, Florida State Museum). The sediment trap estimate is 43% greater than the ^{210}Pb estimate, but this difference is probably within the range of horizontal variation within the lake and annual variations due to changing lake levels. The sediment trap measurements were obtained during a lake level rise of $\sim$2 ft, when plant litter from formerly terrestrial areas would be incorporated into the expanding littoral zone of the lake. Thus pelagic sedimentation rates would logically be higher during rising water levels than when lake level remains fairly constant.

Second, although the annual atmospheric phosphorus loading rate (44–58 mg $P/m^2 \cdot yr$) is much lower than the measured phosphorus sedimentation rate (370 mg $P/m^2 \cdot yr$), the trap results provide a gross annual rate that is applicable only to an undefined part of the pelagic zone. A correction can be applied to account for phosphorus release from the sedimented particulate matter, based on the difference between TP in surface sediments and TP in particulates retained in the traps. Surface sediments contain about 0.034% phosphorus (dicussed later in this chapter), while the sedimenting material contained approximately 0.085% phosphorus. Thus 60% of the phosphorus in sedimenting material appears to be returned to the water column. Net phosphorus sedimentation therefore would be $\sim$150 mg/$m^2 \cdot yr$, which is 2.6 to 3.4 times the atmospheric phosphorus input.

The third observation that indicates sedimentation rates are higher in the deeper areas of the lake relates to patterns of sediment accumulation in the McCloud Lake basin. Extensive emergent and submergent macrophyte communities are found along the shore and in the

shallow littoral areas, although very little organic sediment accumulation is noted there. On the other hand, pelagic sediments are as much as several meters thick (personal communication, Michael Binford) and highly organic (see Chapter 6). Therefore sedimentation rates measured in the middle of McCloud Lake should not be applied to the lake as a whole. At a minimum, these data apply to the area of lake bottom where water depth $\geq$ water depth at which the traps were located ($\sim$4.5 m). At a maximum they represent the area of thick organic sediment accumulation (water depth $\geq \sim$2–2.5 m).

Phosphorus Compartments

Macrophytes. Figure 3-5 shows the extent of coverage by macrophyte beds in McCloud Lake on September 30, 1982. This figure delineates the areas of relatively uniform and continuous coverage by Websteria and Eleocharis. Although emergent species (e.g., Leersia, Fuirena, and Xyris) predominated shoreward of the submergent beds, sparse Websteria stands commonly were observed among these emergents. Likewise, Eleocharis beds did not end abruptly at the deeper border indicated in Figure 3-5. The density of the Eleocharis bed decreased with depth until coverage was no longer complete, but scattered "clumps" of various sizes were observed even in the deepest areas of the lake. This figure and subsequent discussions therefore represent conservative estimates of the importance of Websteria and Eleocharis in McCloud Lake.

These two species covered about 14,000 m^2, or 26% of the total lake bottom. Eleocharis comprised the majority of macrophyte coverage (93%), and as Table 3-7 shows, this species also contained a much larger proportion of phosphorus than Websteria. Although the density

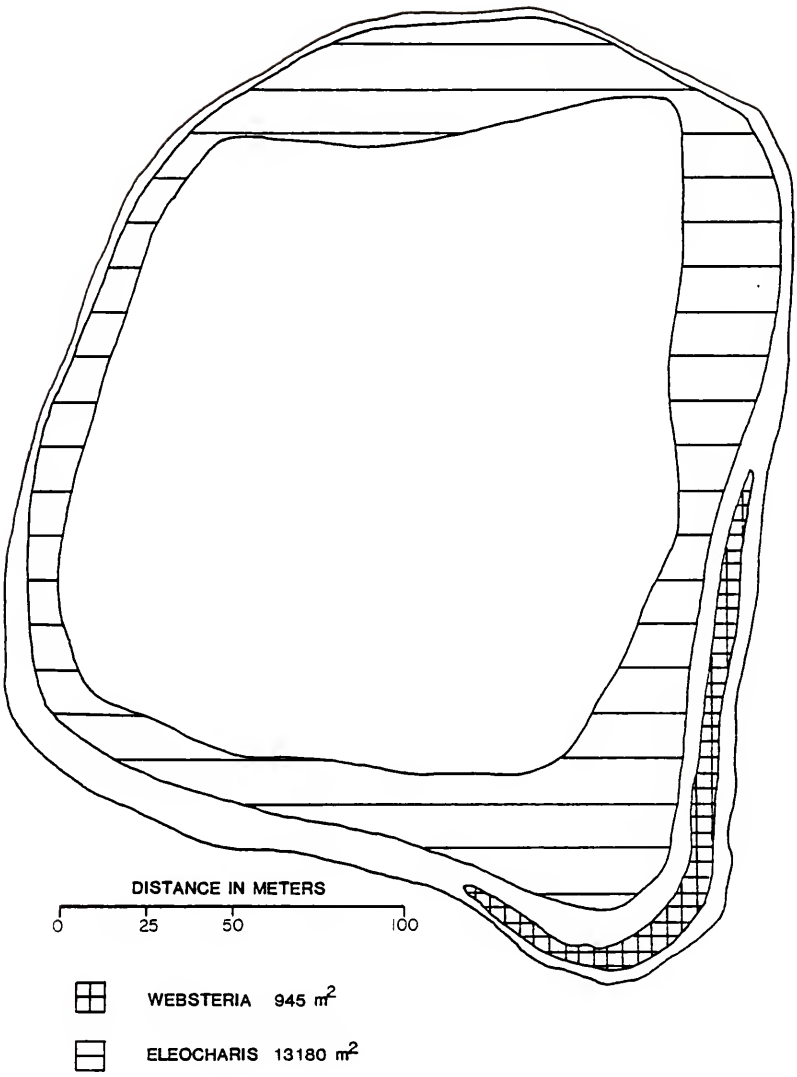

Figure 3-5. Extent of submerged macrophyte coverage in McCloud Lake, September 1982.

Table 3-8. Physical characteristics and phosphorus content (mean and standard deviation) of submergent macrophytes in McCloud Lake, September 30, 1982.

	Eleocharis	Websteria
Dry Weight (g/m^2)	39.8 ± 28.5	ND*
Volatile Solids (g/m^2)	25.6 ± 17.6	ND*
Phosphorus (mg/g dry wt)	7.27 ± 1.01	1.45 ± 0.033

*Not determined.

of Websteria beds was not measured separately, these plants tended to be much shorter and to provide a sparser cover than the Eleocharis. Eleocharis therefore constituted a much larger in-lake phosphorus storage than did Websteria. Using average values from Table 3-7, the total Eleocharis biomass contained about 3.81 Kg of phosphorus, which was 2.5 times the amount of dissolved and particulate phosphorus present in the water column of the lake at that time.

The significance of macrophyte phosphorus storage to water column processes depends on the source of phosphorus which these plants utilize. If they obtain most of their phosphorus from the water, then Eleocharis and Websteria compete with planktonic primary producers, but if the sediments supply their phosphorus, the macrophytes represent a significant mechanism of sediment phosphorus mobilization. Carignan and Kalff (1980) used ^{32}P-labeled sediments to determine whether nine rooted aquatic macrophyte species obtained their phosphorus from sediments or water during in situ incubations in Canadian lakes. They found that sediments were the only significant source of phosphorus to the macrophytes in oligotrophic and mildly eutrophic lakes that had relatively high interstitial phosphorus concentrations. Barko and Smart (1980) obtained similar results with laboratory incubations of three species of submersed macrophytes with minor root systems. They further concluded that release of phosphorus from these species to the water column was a result of tissue decay instead of excretory processes. It thus appears that Eleocharis and Websteria do not compete with phytoplankton for phosphorus in McCloud Lake. However, based on the phosphorus stored in these macrophytes, they represent a potentially

important mechanism for returning sediment phosphorus to the lake when they senesce and die.

Sediments. Surface sediment in the center of McCloud Lake is highly organic with a large proportion of water (Table 3-8). The phosphorus content of this surficial sediment is about 0.34 mg/g dry weight. If these sediment characteristics are typical where lake depth is 8 feet or greater (the approximate extent of macrophyte beds), the upper 1 cm represents a storage of approximately 7.74 Kg of phosphorus. This is about 5 times the mean phosphorus storage in the lake water (1.54 Kg P), and 2.7 to 3.5 times the annual total atmospheric phosphorus loading to the lake surface.

Phosphorus Uptake

Results of the phosphorus uptake experiments using the two major groups of primary producers in McCloud Lake are summarized in Table 3-9. Even though mid-lake seston showed a first-order uptake rate constant (k) nearly twice the magnitude of the k value for Websteria, the variability in seston uptake rendered the two mean k values statistically indistinguishable (t-test, $\alpha < 0.05$). The fact that rooted submergent macrophytes appear to obtain most of their phosphorus from the sediments indicates that there is no competition for phosphorus between the macrophytes and planktonic algae.

Summary

The pH of McCloud Lake has decreased from 4.85 to about 4.55 over the past 15 years (nearly a doubling of H^+ concentration), although this has not been accompanied by a reduction of TP, chlorophyll-a, or other nutrient species. The lake exhibits TP, chlorophyll-a, and

Table 3-9. Physical characteristics and phosphorus content of surficial mid-lake sediment from McCloud Lake.

Parameter	Mean	Standard Deviation
Water, %	93.03	0.18
Volatile Solids, %	77.7	1.00
Phosphorus, mg P/g dry wt	0.343	0.027
Phosphorus, %	0.034	0.003
Interstitial TP, mg/L	0.045	0.004

Table 3-10. Phosphorus uptake rate constants (mean ± standard deviation) for submergent macrophytes and mid-lake seston from McCloud Lake.

Component	Uptake Rate Constant (k), hr^{-1}	n
Mid-Lake Seston	0.486 ± 0.364	4
Websteria sp.	0.257 ± 0.064	3

$t = 1.05$; $t_{.05,5} = 2.57$.

phytoplankton and zooplankton communities that are typical of oligotrophic Florida lakes. Nitrogen-to-phosphorus ratios indicate that primary production is limited by phosphorus. Total phosphorus shows increased concentrations during late spring and summer, but SRP trends are not evident.

Nutrient levels during 1980–1982 appear to be related to rainfall patterns and variations in lake stage. This trend is consistent with the finding (Baker 1984) that rainfall to the lake surface accounts for 90% of the total annual water input. Furthermore, atmospheric phosphorus deposition to McCloud Lake appears to approximate the minimum phosphorus loading rate required to sustain mesotrophic conditions, although the lake is oligotrophic. This suggests that McCloud Lake's low pH inhibits water column productivity, or that phosphorus removal mechanisms are faster than in the lakes used to develop nutrient loading criteria.

Rooted submersed macrophytes constitute a significant in-lake storage of phosphorus that is approximately 5.0 times the mean water column phosphorus storage. It thus appears that the littoral zone contributes much of the primary production in McCloud Lake, although the macrophytes do not compete with phytoplankton for water column phosphorus. Dense periphytic growths, which were common on the macrophytes, may minimize the role these macrophytes play in recycling sediment phosphorus to the water column. The following three chapters discuss the results of experiments designed to test the effect of lake pH on processes that contribute to removal or recycling of water column phosphorus.

CHAPTER 4
EFFECT OF PH ON PLANKTONIC PHOSPHORUS DYNAMICS

There is ample evidence to suggest that variations in aquatic pH are accompanied by changes in phytoplankton and zooplankton communities and by changes in phosphorus dynamics in the pelagic environment. However, it is difficult to know how these processes relate to each other. Plankton community changes related to acidification could theoretically affect phosphorus cycling, but conversely pH-related changes in phosphorus availability could also affect planktonic community structure. Rates of phosphorus uptake by algae and bacteria generally increase as cell size decreases (Lean and White 1983), and phosphorus regeneration is faster for small zooplankters than for large species (Johannes 1965; Hargrave and Geen 1968; Peters and Rigler 1973). Thus pH-related trends in body size of phytoplankton and zooplankton communities should alter phosphorus dynamics.

On the other hand, the activity of extracellular enzymes used by algae in assimilating phosphorus is influenced strongly by pH. Thus decreased pH could favor phytoplankton species which produce phosphatase enzymes that are active at the new pH value. This scenario would have the greatest potential impact on phytoplankton community structure in phosphorus-limited lakes.

A series of experiments was designed to test the effect of pH manipulation on phytoplankton and zooplankton community structure and on sestonic rates of phosphorus uptake and turnover.

Materials and Methods

Mesocosm (Limno-Enclosure) Experiments

Littoral mesocosms. Three polyethylene enclosures were constructed according to Landers (1979) and installed in the littoral zone (1 m depth) of McCloud Lake in February 1981. Each mesocosm enclosed a 12-m^2 water column, and the polyethylene material was inserted into the sediment and secured with wooden stakes and rope to ensure a good seal. Before pH adjustment began, the mesocosms were allowed to equilibrate for 4 weeks. The pH of enclosure A was decreased to 3.6 over a 4-week period with 1.0-L additions of 0.7 N H_2SO_4, while the pH of enclosure B was raised in the same manner to >5.1 with 1.0-L additions of 0.1 to 0.4 N NaOH. Further acid and base additions were made as necessary to maintain the desired pH ranges, although enclosure B never reached the intended pH of 5.6 because of buffering by the sediments (Baker 1984). Enclosure C was left at the ambient pH (4.6 $\pm$ 0.1) throughout the experiment. These mesocosms were sampled on a weekly basis to follow changes in the littoral chemistry and biology resulting from pH alteration. In addition, a littoral lake station adjacent to the enclosures was sampled on the same schedule. Chemical and biological analyses were performed as described in Chapter 3.

Mid-lake mesocosms. Six enclosures were placed in the middle of the lake in July 1982 to evaluate the effects of acidification and

nutrient addition on phosphorus dynamics and phytoplankton and zooplankton communities. Two groups of three enclosures were installed 1 week apart. These mesocosms were 0.92 m in diameter, 2.2 m deep, and each contained 1.2 m^3 of depth-composited lake water (added with a gasoline-powered pump). The pH treatment in these enclosures consisted of duplicates at each of three values: M1 and M4 were left at the lake pH of 4.7; M2 and M5 were lowered to 4.1 with 0.1 N H_2SO_4; and M3 and M6 were first lowered to 4.1 and then further acidified to 3.7 1 week later. No additional pH adjustment was required since the enclosures were isolated from the sediments. During the tenth week after pH adjustment, NH_4-NO_3 and KH_2PO_4 were added to enclosures 1–3 to increase TN and TP each by a factor of about 10. These enclosures and a mid-lake station were sampled twice each month from the end of July through November 1982 using the previously described methods for sample collection and analysis (Chapter 3).

Radiolabeled orthophosphorus (^{32}P) was used to measure sestonic uptake and turnover of phosphorus in the mid-lake enclosures. One-liter samples of seston (unfiltered water) from each enclosure were transported to the laboratory and incubated at room temperature (22°C $\pm$ 2°C) in clear glass bottles. Fluorescent lighting was provided from above, and magnetic stirrers slowly mixed the contents. Aliquots of a stock solution containing K_2HPO_4 as a carrier for $^{32}PO_4$ (obtained from New England Nuclear) were added to the seston samples, and uptake of added ^{32}P was followed by periodically filtering 5-mL subsamples (0.45 µm membrane filters). The volume of stock added in each experiment was adjusted according to its specific activity, but the range was 25 µL to 1000 µL stock/L sample. The stock solution contained 3.1 µg

P/mL, and the activity introduced to each sample yielded approximately 12,000–60,000 counts per minute (CPM) in the 5-mL subsample. The filter and filtrate were stored in separate scintillation vials until they were counted on a Packard Tri-Carb model 4530 liquid scintillation counter. Counts were corrected for background activity and decay so that results corresponded to the time at which samples were collected. Total SRP was calculated as SRP originally in each enclosure plus the amount added in the laboratory.

A similar design was used to measure directly the release of phosphorus by seston from the mid-lake enclosures. A 2-L sample was collected from each enclosure and transported immediately to the laboratory. The seston was concentrated by a factor of 10 by vacuum filtering all but a small volume (∿20 mL) through 0.45 μm membrane filters. This concentrated volume was transferred to an Erlenmeyer flask, and seston retained on the filter was resuspended by vortexing three times in 10 mL of filtered enclosure water. The resuspended seston was added to the Erlenmeyer and additional filtered water was used to obtain a final volume of 200 mL. Stock radiophosphorus was added and the flasks were incubated under fluorescent lighting for 24 h to allow uniform labeling of the seston. After the incubation period, the seston was again concentrated by a combination of centrifugation and vacuum filtration of the supernatant. The concentrated, labelled seston (∿10 mL) was added to unlabelled filtered enclosure water to obtain a volume of 500 mL. Phosphorus release was followed by periodically filtering 5-mL aliquots (0.45 μm membrane filters), and storing filter and filtrate in separate scintillation vials for later analysis with the liquid scintillation counter.

Several methods have been used for quantifying phosphorus uptake and turnover. Many ^{32}P users have adopted a method described by Zilversmit et al. (1943) for calculating uptake rates and turnover times in radioisotope experiments. The method necessitates three assumptions:

1) Steady state conditions in which the rate of appearance of the isotope equals its rate of disappearance;
2) Constant rate of appearance and disappearance; and
3) Random appearance and disappearance of the element and its isotope.

They further define:

p = rate of disappearance of B from fluid;

x = amount of radioactive B in the fluid at any time;

r = total amount of B present in fluid (assumed to be constant); and

t_t = turnover time, the time required for the tissue to completely remove and replace r.

The change in x with time is given as

$$dx/dt = -p(x/r). \qquad \text{(EQ 1)}$$

Integrating EQ 1 yields

$$x/r = ce(-p/r^t) \qquad \text{(EQ 2)}$$

and taking natural logarithms, EQ 2 becomes

$$\ln x/r = \ln c - p/r \cdot t \qquad \text{(EQ 3)}$$

Equation 3 describes a straight line with slope = $-p/r$ which in turn equals $-1/t_t$. Therefore, from a plot of ln x/r versus time and knowledge of r, both uptake rate and turnover time can be calculated.

Zilversmit et al. (1943) cautioned that their method of uptake and turnover calculations was valid only during the time interval in which none of the radioisotope is returned from the tissue to the fluid. Fast initial uptake of SRP (and thus quick turnover) coupled with the difficulty of measuring accurately the initial SRP concentration led Lean and White (1983) to recommend that first-order uptake rate constants (k) should be used instead. The value of k ($time^{-1}$) can be obtained as the slope of a plot of percent isotope in the filtrate (or the filter) versus time.

Diurnal productivity estimates were made in conjunction with both mesocosm studies by following diel DO changes in the water columns of the enclosures with a YSI model 57A dissolved oxygen meter. Oxygen measurements in the littoral enclosures were made at 2- to 5-h intervals over 24-h periods, with shorter intervals used in early morning and early evening, when DO changes occurred most rapidly. Dissolved oxygen was measured every 3 h over 24-h periods in the mid-lake enclosures. Oxygen changes in the open water of both sets of enclosures were corrected for diffusion across the air-water interface with a diffusion coefficient experimentally determined for the lake using the dome method of Copeland and Duffer (1964). Gross primary production (P) and respiration (R) were determined by planimetry from plots of corrected rate of DO change over time as described by Odum (1956) and numerous others (Odum and Hoskin 1958; Hall and Moll 1975) for measurement of community metabolism.

Laboratory Microcosms

An experiment similar to the mesocosms involved microcosms set up in the laboratory in March 1983. Three 12-L glass carboys were filled simultaneously by siphoning from a continuously stirred 40-L container of depth-composited lake water. The microcosms were aerated slowly to provide mixing, and overhead fluorescent lighting was timed to mimic the natural day length. One microcosm was left at ambient pH (4.60), and 1 N H_2SO_4 was used to achieve pH values of 4.0 and 3.6 in the other two. SRP, TP, and total dissolved phosphorus (TDP) were measured periodically using previously described methods. Because of an accidental shift in TN/TP ratios, this experiment was terminated 4 weeks after pH adjustment.

Three new microcosms were set up in the same manner in May 1983. Two weeks after pH adjustment, NH_4-NO_3 and NaH_2PO_4 solutions were added to increase TN and TP to $\sim$1.0 mg/L and 0.1 mg/L, respectively. TP, TDP, and SRP were measured periodically before and after nutrient addition. The activity of extracellular acid phosphatase enzymes was measured in the microcosm experiments by a fluorometric method developed by Swedish limnologists (Petterson and Jansson 1978; Jansson et al. 1981; Jansson 1981). The procedure involves addition of a buffered fluorogenic substrate (4-methylumbelliferyl phosphate, MUP) to the water sample. Phosphomonoesterase activity is calculated from the rate of liberation of fluorescent hydrolysis product 4-methylumbelliferone (MU). Fluorescence of MU was determined with an American Instrument Co. SPF-125 spectrofluorometer using an excitation wavelength of 320 nm and an emission wavelength of 450 nm. A stock solution of 10^{-2} M MUP was prepared in autoclaved distilled water and

frozen in 1-mL crimp-seal vials until needed. Working MUP solutions (10^{-4} M) were obtained by dilution of the stock in 0.1 M acetate buffer at each microcosm pH (4.6, 4.0, and 3.6). For the assay, 0.5 mL of working MUP solution was added to 4 mL of the test water. Thus the test could be run at the pH of each sample, or all microcosms could be tested at pH 4.6. The amount of fluorescent MU released was quantified by comparison to standard MU solutions prepared in acetate buffer.

Results and Discussion

Littoral Mesocosms

Figure 4-1 shows variations in soluble reactive phosphorus in the littoral enclosures over 15 weeks (including 4 weeks of pH adjustment but not the initial 4-week equilibration after installation). Figure 4-2 shows total phosphorus variations over the same period. Peaks in SRP occurred in all three enclosures during initial pH adjustment, although the increase was smallest in the control enclosure (C) left at ambient pH. Thereafter, enclosure B (pH = 5.1) often showed the highest SRP concentration, although no consistent trend was evident. Total phosphorus concentrations also were high initially, and then varied in the range 1—10 μg/L after the first 4 weeks. With few exceptions, TP was consistently higher in the high pH enclosure (B) than in the acidified one (A), after initial pH adjustment.

Table 4-1 summarizes mean nutrient concentrations in the littoral enclosures and at the littoral lake station from late March to July 1981. TP shows a trend apparently related to pH, with the highest mean in the base-treated enclosure (13 μg/L), the lowest in the acid treat-

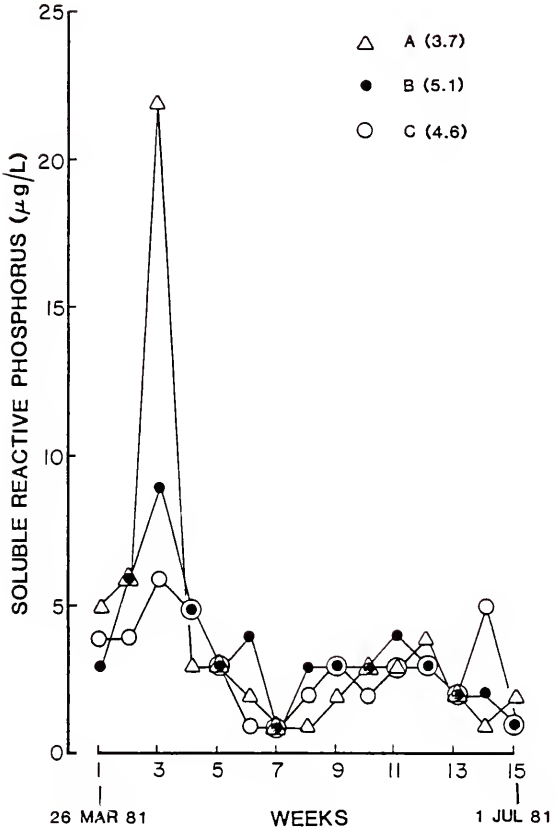

Figure 4-1. Soluble reactive phosphorus variations in littoral mesocosms.

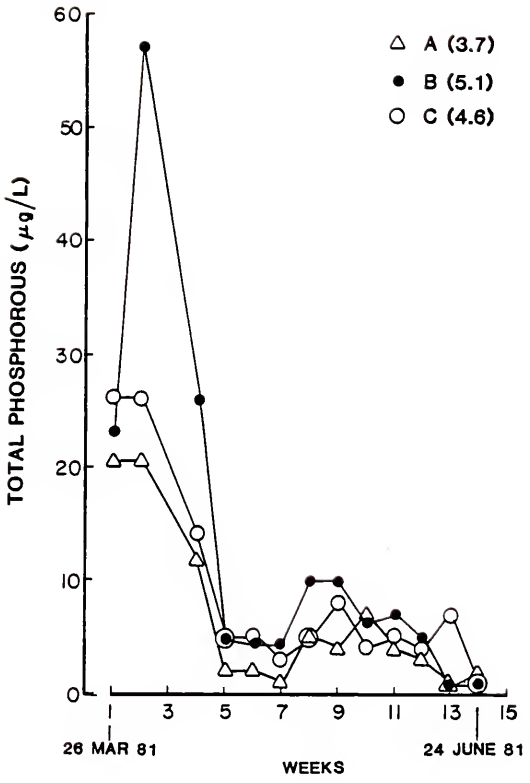

Figure 4-2. Total phosphorus variations in littoral mesocosms.

Table 4-1. Nutrient means (µg/L except TN/TP) in the littoral enclosures.

Parameter	Enclosure A	Enclosure B	Enclosure C	Littoral Lake
SRP	4	4	8	3
TP	7	13	9	12
TN/TP (wt/wt)	54.6	31.0	36.0	45.5
TON	281	357	258	442
NH_4^+-N	49	27	29	50
NO_3^--N	52	27	37	54
NO_2^--N	1	1	1	1

ment (7 µg/L), and 9 µg/L in the ambient pH enclosure. The means are not significantly different (ANOVA, $\alpha > 0.05$); however, analysis of the average TP differences (calculated for each sampling date) between pairs of enclosures (paired-difference t-test) shows that TP was significantly higher in enclosures B and C than in the acidified enclosure ($TP_B - TP_A$, $\alpha = 0.0396$; $TP_C - TP_A$, $\alpha = 0.0138$). The mean difference between B and C is not significant ($\alpha > 0.05$).

Mean TN/TP ratios in the littoral enclosures ranged from 31.0 in the base treatment to 54.6 in the acid treatment, while in the littoral lake the ratio was 45.5 (Table 4-1). These values all indicate phosphorus limitation (TN/TP > 30 according to Huber et al. 1982), and they are similar to mean annual ratios for the mid-lake station (Table 3-1). The trend of increasing TN/TP values as pH decreases suggests that phosphorus becomes more limiting as pH is lowered. This reflects the fact that TN variations in the littoral enclosures were insignificant, while TP decreased with decreasing pH.

Although TN means did not vary significantly in these enclosures, means of some of the nitrogen forms did suggest a pH effect. TON levels did not appear to be related to pH, and the differences among enclosure means were not significant (ANOVA, $\alpha > 0.05$). However, ammonium and nitrate means were slightly higher in the littoral lake than in the enclosures. Both ions tended to increase as enclosure pH decreased, which could indicate increased mineralization or decreased utilization rates, although the differences between treatments were not significant.

Among biological parameters measured in the littoral enclosures, only zooplankton abundance varied significantly. Differences in the

mean values of log-transformed chlorophyll-a and total phytoplankton abundance were not significant (ANOVA, $\alpha > 0.05$), although total phytoplankton means did decrease with decreasing pH. Means of total zooplankton and copepod abundances (log-transformed) also decreased with pH. In both cases the differences between enclosures B and C were not significant, while the values in enclosure A were significantly lower (Duncan's Multiple Range Comparison Test, $\alpha = 0.05$). The variations in total zooplankton numbers were due to the reduction in copepods as pH decreased, as evidenced by the fact that cladoceran and rotifer abundances did not show a treatment effect.

Mid-Lake Mesocosms

Nutrient trends. Figure 4-3 shows TP variations in the unfertilized mid-lake enclosures. TP stayed relatively constant in M1 (control) while it increased in acidified enclosures M2 and M3. In the other set of enclosures however, TP was consistently lower in M6 (pH = 3.7) than in the higher pH enclosures M4 and M5. TP trends were not similar in the control enclosures (M1 and M4). Table 4-2 summarizes the mean nutrient concentrations in the mid-lake enclosures by pH treatment. Total phosphorus was lowest at pH 3.7 (6 µg/L), and was nearly the same at 4.1 (10 µg/L) and 4.7 (9 µg/L). According to Duncan's Multiple Range Test ($\alpha = 0.05$) the two higher TP means did not differ significantly, while both were statistically higher than TP at the low pH of 3.7. SRP concentrations were consistently low in these enclosures and mean SRP was 2 µg/L for all three pH treatments.

TN/TP ratios in the mid-lake enclosures (Table 4-2) were lower than in the littoral enclosures or the lake, and they were indicative

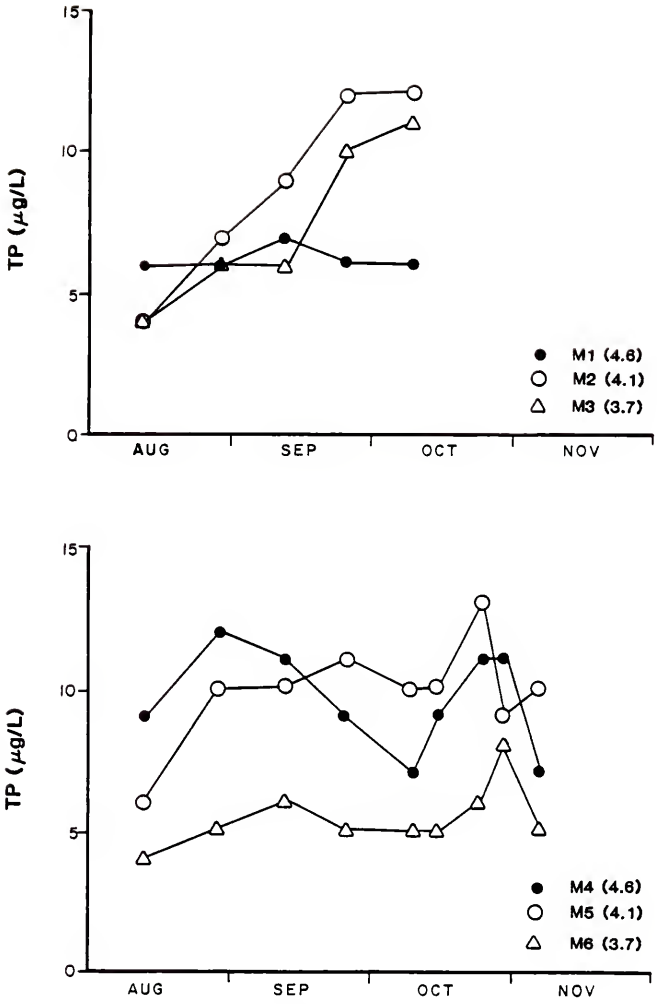

Figure 4-3. Total phosphorus in mid-lake mesocosms, excluding period of nutrient addition.

Table 4-2. Nutrient means (μg/L except TN/TP) for mid-lake enclosure pH groups (excluding data from M1 to M3 after nutrient addition.

Parameter	pH Group 4.6	4.1	3.7
SRP	2	2	2
TP	9	10	6
TN/TP (wt/wt)	15.4	11.5	17.3
NH_4^+-N	11	11	13
NO_3^--N + NO_2^--N	12	7	8
TN	139	115	104

of nutrient-balanced conditions according to criteria proposed for Florida lakes ($10 < TN/TP < 30$; Huber et al. 1982). While the lowest pH enclosures did show the highest TN/TP ratio (17.3), the inverse relationship found between TN/TP and pH in the littoral enclosures was not seen in the mid-lake mesocosms.

Total nitrogen in the unfertilized mid-lake enclosures was highest at the ambient pH (139 µg/L) and decreased with enclosure pH. ANOVA showed a significant treatment (pH) effect ($\alpha < 0.05$), and Duncan's Multiple Range Test yielded the following relationship among mean TN values:

pH 4.7	pH 4.1	pH 3.7

(TN means at underlined pH values are not significantly different, $\alpha = 0.05$). Means of ammonium and nitrate/nitrite were all less than 15 µg/L, and no pH-related trends were evident for these nitrogen forms.

Figure 4-4 illustrates the effect of nutrient addition on the phosphorus fractions in mid-lake enclosures M1, M2, and M3. SRP removal rates were similar in all three pH treatments, and SRP concentrations decreased to pre-fertilization levels within 13 days after nutrient addition. Particulate organic phosphorus (POP) also responded in a similar manner at the three pH values. POP reached maximum levels ($\sim$ 30 µg/L) about 2 weeks after nutrient addition, and had returned to pre-fertilization concentrations within 33 days. The response of soluble organic phosphorus (SOP) did indicate a pH effect, however. SOP in M1 (pH 4.6) and M2 (pH 4.1) stayed below 10 µg/L after nutrient addition, but at the lowest pH (3.7), SOP increased to nearly 30 µg/L.

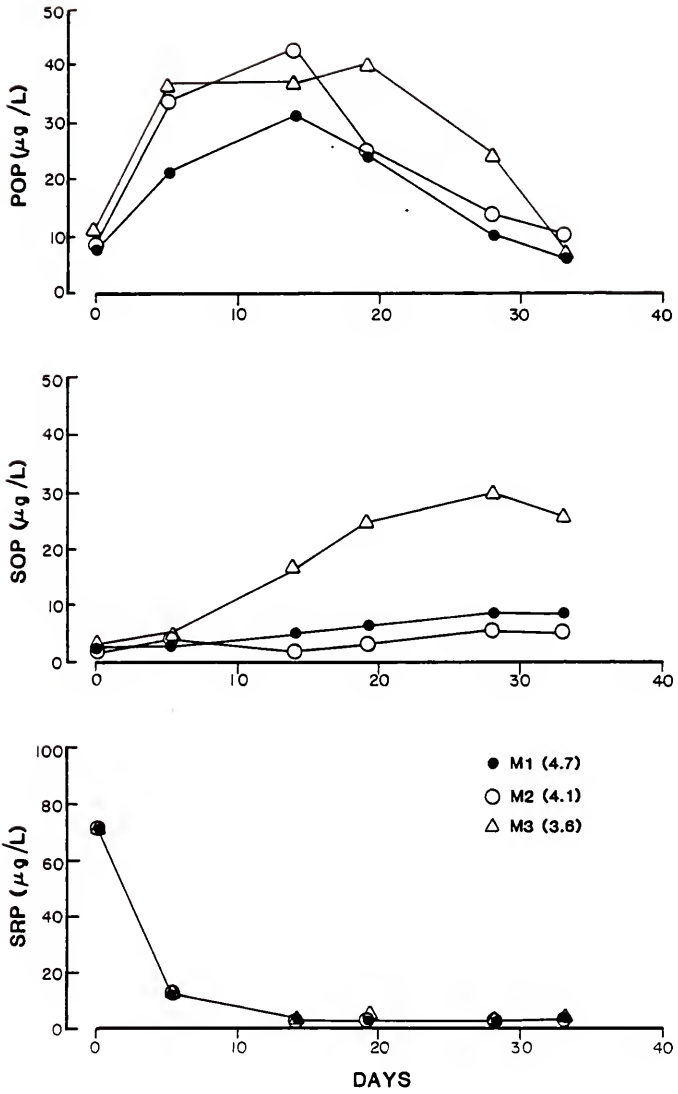

Figure 4-4. Changes in phosphorus forms after nutrient addition to M1, M2, and M3.

These results suggest a reduced ability of the biota to utilize SOP at a pH of 3.7.

Biological trends. Total phytoplankton densities initially decreased in all six mid-lake enclosures, but in the intermediate pH (4.1) enclosures, phytoplankton then began to increase relative to the other enclosures. After nutrient addition to M1, M2, and M3, phytoplankton in both pH 4.1 enclosures (M2 and M5) declined to levels comparable to those in the other enclosures. The addition of nutrients was not followed by an increase in phytoplankton numbers in M1, M2, and M3, although chlorophyll levels did reflect the increased nutrient concentrations. This phenomenon was apparently the result of intensified zooplankton grazing in the fertilized mesocosms, which kept phytoplankton numbers low while production was high. Chlorophyll-a concentrations did increase because the analysis included material extracted from phytoplankters and zooplankters. Total zooplankton populations also increased markedly during the same period in the fertilized enclosures.

Species composition of phytoplankton and zooplankton communities responded to increased acidity in the mid-lake enclosures. Ultraplankton (1–10 μm) comprised 80–100% of total phytoplankton numbers at the lake pH (4.6), but decreased in importance at lower pH values. The green alga Oocystis gloeocystiformis increased in abundance at reduced pH in the unfertilized enclosures, while after fertilization, Cryptomonas marsonii dominated at all three pH values.

Zooplankton response to reduced pH was similar to that seen in the littoral enclosures. Copepod numbers (predominantly Diaptomus mississippiensis) decreased markedly as pH was lowered, so that this group

accounted for less than 1% of total zooplankton in the pH 3.7 mesocosms shortly after initial pH adjustment. The acid-tolerant cladoceran genera Eubosmina and Diaphanosoma became increasingly important at more acidic pH values. Rotifer percent composition in the low pH enclosures increased shortly after pH reduction, but after about 6 more weeks, their importance decreased to levels comparable to the higher pH enclosures. In contrast to phytoplankton composition, zooplankton species composition was not affected by nutrient addition.

Radiophosphorus experiments. Phosphorus uptake by seston in the mid-lake enclosures was measured on six dates using radiolabelled phosphorus in the laboratory. In Figures 4-5 through 4-10, uptake of ^{32}P is represented as the increase in radioactivity on filters versus time during the incubations. (Note variations in abscissas and ordinates on different dates.) The first two dates (Figures 4-5 and 4-6) were before nutrient addition to M1–M3, while the last four were after the addition. Missing data for M1, M4, and M5 in Figures 4-9 and 4-10 (the last two dates) were because bird droppings had caused increases in pH and TP in those enclosures. Mesocosm M1 (pH 4.6) showed the fastest uptake of ^{32}P before nutrient addition, but M6 (pH 3.7) consistently exhibited the fastest uptake after the addition.

Table 4-3 gives uptake rates and turnover times calculated according to Zilversmit et al. (1943) from the data presented in Figures 4-5 through 4-10. Uptake rates ranged from 0.1 to 12 µg/L·h, while the range of turnover times was 0.3 h to 12.2 h. It is interesting to note that the unfertilized mesocosms with the lowest TP values (M1 before nutrient addition, and M6) showed the fastest uptake rates.

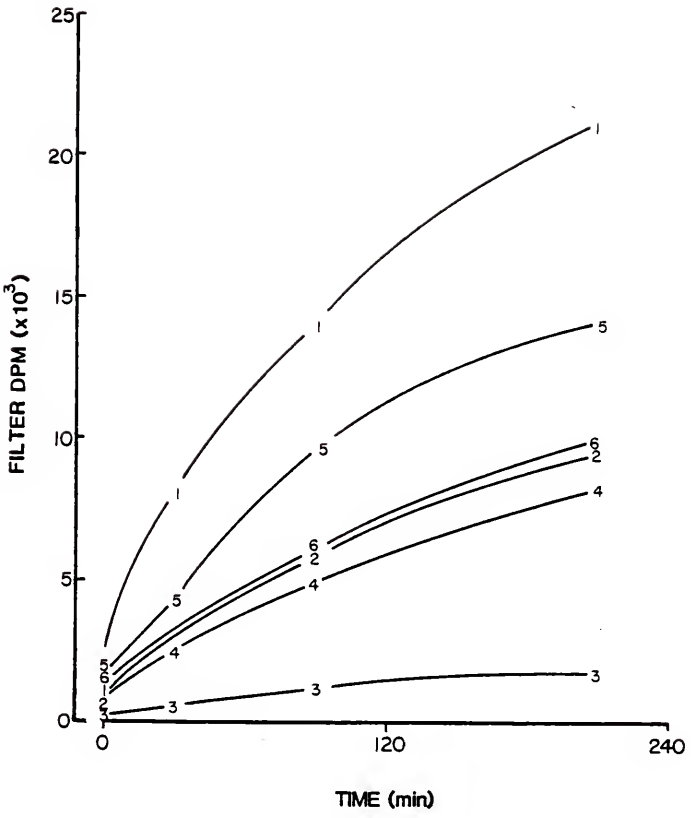

Figure 4-5. ^{32}P uptake by mid-lake enclosure seston, 8/24/82.

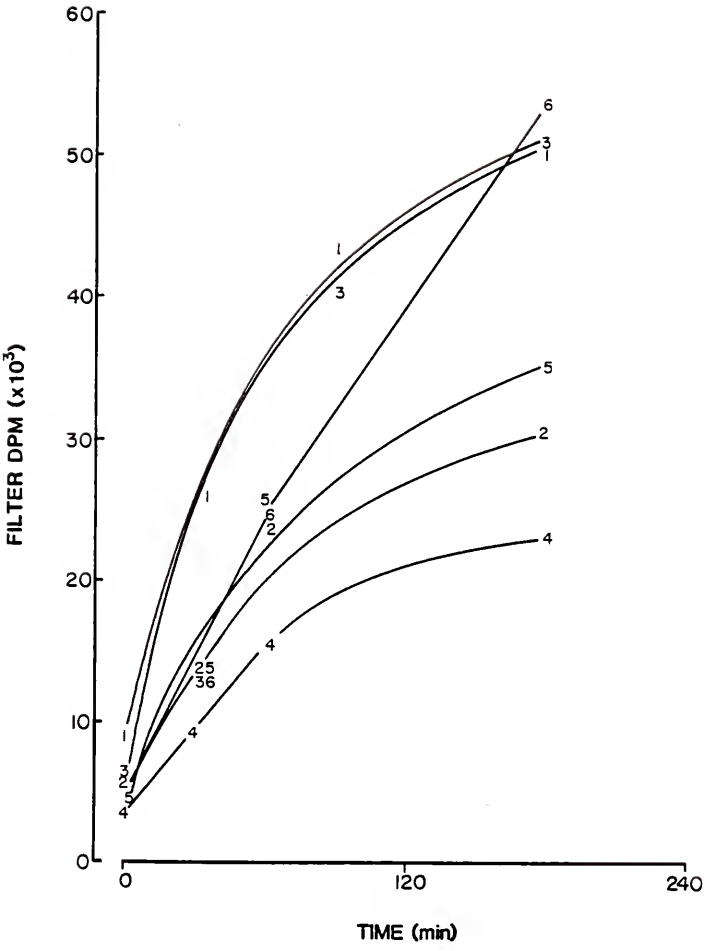

Figure 4-6. ^{32}P uptake by mid-lake enclosure seston, 9/14/82.

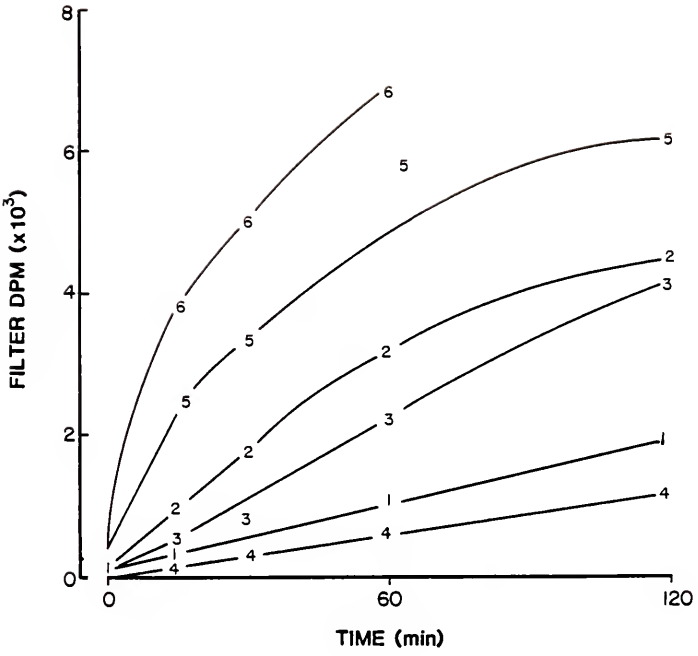

Figure 4-7. ^{32}P uptake by mid-lake enclosure seston, 11/9/82.

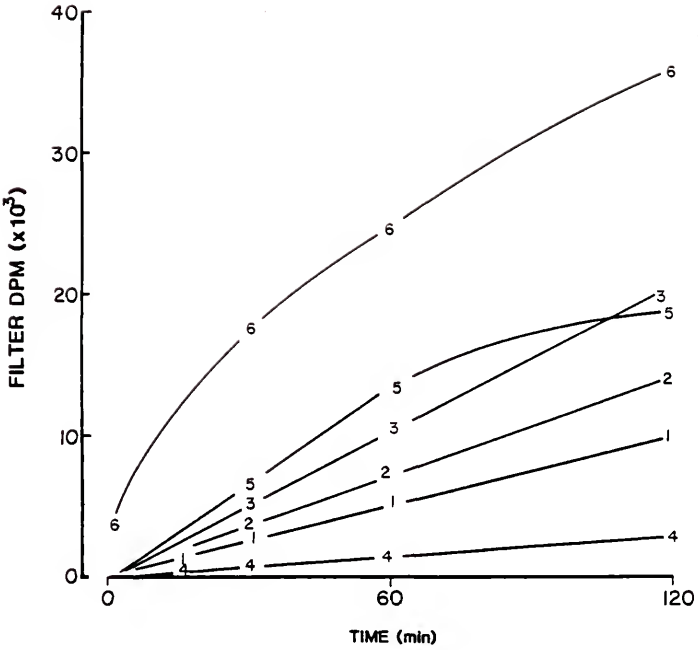

Figure 4-8. ^{32}P uptake by mid-lake enclosure seston, 11/11/82.

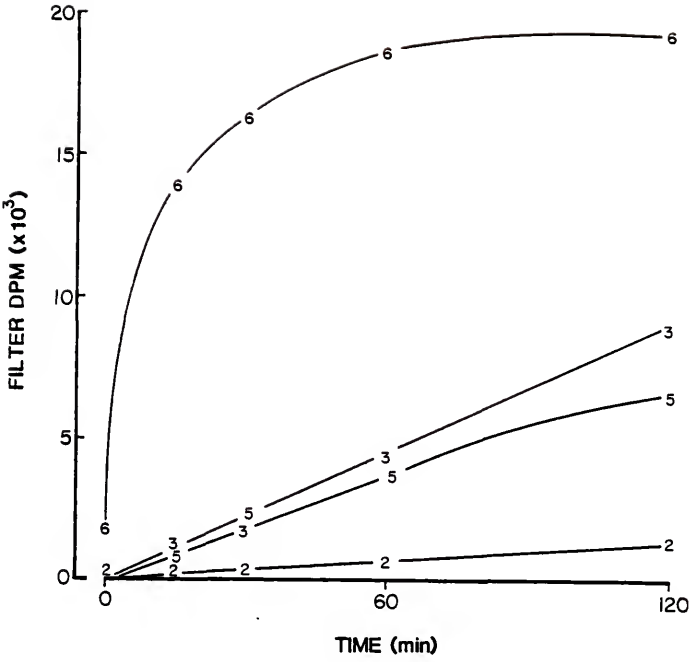

Figure 4-9. ^{32}P uptake by mid-lake enclosure seston, 11/18/82.

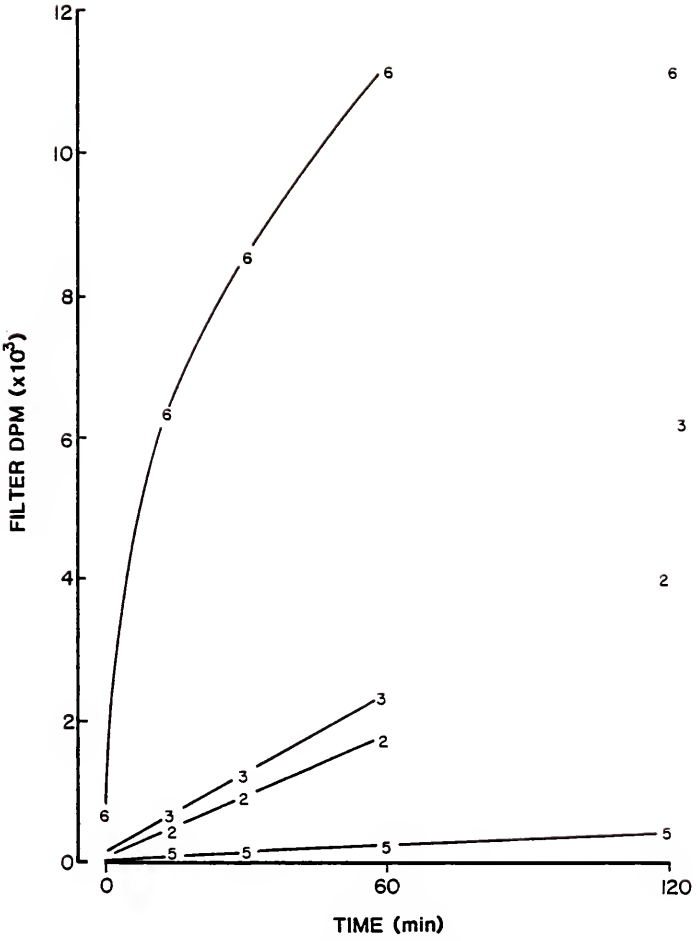

Figure 4-10. ^{32}P uptake by mid-lake enclosure seston, 11/23/82.

Table 4-3. Phosphorus uptake rates and turnover times by seston from mid-lake enclosures (underlined values indicate enclosures with nutrient addition).

Date	Var.	M1	M2	M3	M4	M5	M6
08/24	p	12	1.8	0.6	2.4	4.2	2.4
	t_t	0.4	3.9	10.0	3.3	1.2	1.7
09/14	p	6	3.0	3.6	1.2	2.4	4.2
	t_t	0.5	1.0	0.8	1.7	1.2	0.5
11/09	p	0.6	4.8	1.8	0.2	2.4	4.2
	t_t	6.2	1.2	2.0	9.4	0.7	0.6
11/11	p	0.4	0.2	1.2	0.1	1.2	1.2
	t_t	9.7	9.2	5.8	28.0	3.3	2.7
11/18	p	--	0.2	0.6	0.6	1.8	11.0
	t_t	--	12.2	11.6	2.8	2.2	0.3
11/23	p	--	0.5	0.4	--	--	6
	t_t	--	7.4	5.6	--	--	0.7

p = Uptake rate ($\mu g/L \cdot h$).
t_t = Turnover time (h).

The same procedure was used to calculate phosphorus release rates from the seston concentration experiments, which were carried out on two dates before nutrient addition to enclosures M1, M2, and M3. These release rates, corrected to reflect the original seston concentrations, are given in Table 4-4. No effect of enclosure pH is evident in these data, although the range of values is comparable to the uptake rates in Table 4-3.

Table 4-5 lists the means and ranges of uptake rate constants calculated by the method of Lean and White (1983) from the same experimental data presented in figures and tables above. Results using this method were similar to those of the previous method. In the group consisting of M4, M5, and M6 there was a clear trend of increasing rate constants as pH decreased. However, this was not repeated in the prefertilization data for M1, M2, and M3, where the high pH enclosure (M1) showed the largest rate constants. ANOVA revealed no significant effect of pH on k values ($\alpha > 0.05$). It thus appears that phosphorus availability has more effect on the planktonic uptake and turnover of phosphorus than does any direct effect of hydrogen ion concentration. Furthermore, phosphorus availability (as indicated by SRP concentrations) did not appear to be related to pH in these mesocosms.

Community Metabolism

The diel oxygen technique was used to obtain two estimates of community metabolism in the littoral enclosures, while the mid-lake enclosures were monitored on three dates. Table 4-5 presents means of these productivity (P) and respiration (R) measurements for the littoral and

Table 4-4. Phosphorus release rates (μg/L·h) by seston from mid-lake enclosures.

Date	Enclosure					
	M1	M2	M3	M4	M5	M6
08/27	2.0	10.2	0.5	0.7	0.6	1.7
09/16	2.1	0.7	3.2	--	2.1	0.5

Table 4-5. Phosphorus uptake rate constants (h^{-1}) for the mid-lake enclosures.

Enclosure	pH	Mean k	Range
M1 (Pre)	4.6	0.74	0.52-0.96
M1 (Post)	4.6	0.11	0.09-0.13
M2 (Pre)	4.1	0.25	0.14-0.36
M2 (Post)	4.1	0.25	0.13-0.50
M3 (Pre)	3.7	0.32	0.02-0.61
M3 (Post)	3.7	0.28	0.19-0.37
M4	4.6	0.14	0.02-0.32
M5	4.1	0.40	0.01-1.30
M6	3.6	1.12	0.17-1.99

mid-lake mesocosms, and a mid-lake station adjacent to the open-water enclosures. The data are expressed on a volumetric basis (g $O_2/m^3 \cdot day$) to allow comparison of metabolism in communities of different depth (Lind and Campbell 1970).

P and R means were similar in any given enclosure. Mean productivity in the mid-lake mesocosms ranged from 0.70 to 0.84 g $O_2/m^3 \cdot day$, while mean respiration varied from 0.75 to 1.01 g $O_2/m^3 \cdot day$. Average P/R ratios were close to unity in these communities and at the mid-lake station. Two-way ANOVA and Duncan's Multiple Range Comparison showed no significant pH effect on P, R, or P/R ratios for the enclosures, and no significant differences in these parameters between the open lake and any enclosure.

Total community P and R were much higher in the littoral enclosures than in the open lake or the mid-lake enclosures. Mean P ranged from 3.8 to 6.1 g $O_2/m^3 \cdot day$ and the range in R was 3.8 to 7.1 g $O_2/m^3 \cdot day$. The difference between littoral and open lake communities probably reflects the contribution of submersed macrophytes and periphytic algae to littoral productivity. It is interesting to note that the higher littoral primary productivity was balanced by a comparable community respiration, so that P/R ratios were near 1.0 for littoral and planktonic communities. A P/R value near unity is considered indicative of a balanced ecosystem (Lind and Campbell 1970). Two-way ANOVA of the littoral metabolism data showed no significant pH effect ($\alpha > 0.10$ in all cases) on productivity, respiration, or P/R values.

Although areal or volumetric rates of primary productivity are higher in the littoral zone of McCloud Lake than in its pelagic waters, the area represented by both habitats would have to be determined to

Table 4-6. Volumetric productivity (P), respiration (R), and P/R means in littoral and pelagic mesocosms.

Community	pH	n	$\overline{P}$*	$\overline{R}$*	$\overline{P/R}$
Open-water M1	4.6	3	0.70	0.75	1.05
Open-water M4	4.6	3	0.82	0.92	1.01
Mid-lake	4.6	3	0.83	1.01	0.87
Littoral C	4.6	2	6.07	7.12	0.86
Littoral B	5.6	2	4.98	5.36	0.93
Open-water M2	4.1	3	0.84	0.88	1.12
Open-water M5	4.1	3	0.76	0.94	0.83
Open-water M3	3.7	3	0.83	0.88	1.12
Open-water M6	3.7	3	0.77	1.01	0.77
Littoral A	3.7	2	3.82	3.83	1.02

*g $O_2/m^3 \cdot day$.

evaluate the overall importance of each zone to total lake productivity. Variations in primary productivity are matched by similar changes in respiration, so that P/R ratios remain close to unity. In addition, variation of pH between 5.6 and 3.6 did not significantly affect the metabolism of littoral or planktonic communities originally adapted to a pH of 4.6.

Laboratory Microcosms

Total phosphorus concentrations in the unfertilized microcosms were too low (generally 2–4 μg/L) to permit determination of a pH effect. Initial TP levels were higher (∿6 μg/L), but filamentous algae growing on the glass microcosm walls soon reduced the phosphorus available to planktonic biomass. SRP uptake after nutrient addition to the second set of microcosms is shown in Figure 4-11. Removal of SRP from the water columns appeared to follow first order kinetics for 5–6 days, but it was essentially linear from that point through day 15. This could be accounted for by a 5–6-day lag in the increase of zooplankton numbers, after which zooplankton grazing would encourage a constant rate of algal productivity.

There was no indication that microcosm pH influenced the rate of SRP uptake, which was essentially identical at the ambient pH (4.6) and the low pH (3.7), and was only slightly slower at the intermediate pH. In addition, the shapes of SRP loss curves were the same at all three pH values.

After fertilization, these microcosms did not exhibit the SOP increase at pH 3.7 that was seen in the mid-lake mesocosms. The large surface-to-volume ratio in the microcosms increased the importance of

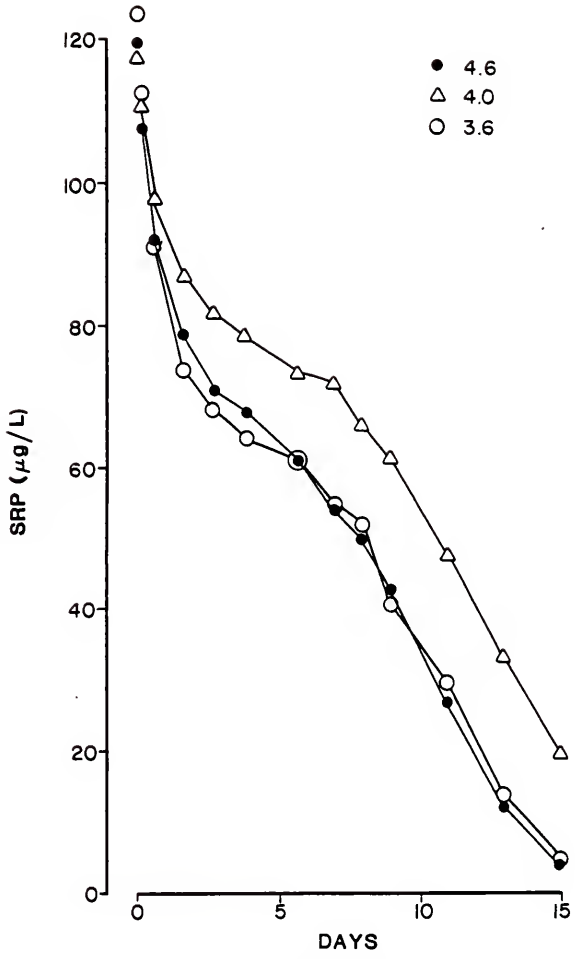

Figure 4-11. SRP in microcosms after nutrient addition.

attached algae, so that the response of water column TP to fertilization was much less at all pH values than in the mid-lake enclosures. Despite the inherent differences between the microcosm and enclosure experiments, microcosm fertilization did indicate that the SOP increase seen in the pH 3.7 enclosure was not a universal effect of low pH. Both experiments also showed little or no effect of pH on SRP uptake.

Acid phosphatase activity. Table 4-7 presents typical phosphatase assay results from the first set of microcosms. Activity decreased as assay pH decreased, regardless of initial pH of the sample, and the potential activity (all assayed at pH 4.7) decreased as microcosm pH decreased. Activity in the two low pH microcosms was 80—150% higher when assayed at pH 4.7 than at the ambient microcosm pH. This indicates that the enzymes were adapted to the ambient pH of the lake, and also suggests that production of the extracellular enzymes decreased at the lower pH values. While pH definitely affected the potential activity of the enzymes, many factors can influence production of phosphatase enzymes.

Potential phosphatase activity in the second set of microcosms showed the same pH effect (Table 4-7). Samples from the acidified microcosms showed higher enzyme activity when assayed at pH 4.7 than at ambient pH. However, enzyme production did not follow the same pattern. When samples from all three microcosms were assayed at pH 4.7 the activity of the pH 3.7 microcosm was frequently equal to or higher than that of the pH 4.7 microcosm, and activity of the intermediate pH microcosm was higher than in either of the other two. These results indicate that some factor (or factors) other than pH affects the production of acid phosphomonoesterase enzymes.

Table 4-7. Effect of pH on phosphatase enzyme activity (n mole/L·min) in microcosm experiments.

	FIRST EXPERIMENT			SECOND EXPERIMENT		
	Microcosm pH			Microcosm pH		
Assay pH	4.7	4.0	3.7	4.7	4.0	3.7
4.7	30.2	16.1	9.1	14.5	24.1	15.1
4.0		6.1			9.3	
3.7			5.1			7.8

CHAPTER 5
EFFECT OF PH ON PHOSPHORUS RELEASE DURING PLANT DECOMPOSITION

Grahn et al. (1974) hypothesized that acidification of fresh waters causes reduced rates of organic matter decomposition and thus slower rates of nutrient remineralization. Experiments to test this hypothesis have taken several forms. Most researchers have examined the effect of pH on loss of particulate or soluble organic substrate, and little attention has been focused on the release of nutrients during decomposition of naturally occurring particulate organic matter. This chapter presents experiments designed to follow release of soluble reactive phosphorus from plant matter decomposing at different experimental pH values. Because the submergent macrophytes Websteria sp. and Eleocharis sp. represent a large reservoir of phosphorus within the lake, they were used as the organic substrate in these experiments.

Experimental Methods

Live, freshly collected Eleocharis or Websteria plants were used in all experiments in order to simulate as closely as possible the conditions of decomposition in McCloud Lake. Intact plants were collected from the littoral zone, brought to the laboratory, and gently washed to remove attached algae from the leaves and organic sediment from the roots. The plants were blotted dry with paper towels to obtain fresh

weights. Representative samples were dried and digested at the beginning of each experiment to obtain water and phosphorus contents.

Preliminary Experiments

In the first experiment Websteria plants were blotted dry and 2.0 g (± 0.01 g) of intact plant material were added to each of 18 glass-stoppered, 300-mL clear glass bottles. The bottles were overfilled with filtered lake water (0.45 μm membrane filters) to eliminate air. No bacterial seed was introduced, as it was assumed that sufficient bacteria were present on the plants.

Additions of 1 N H_2SO_4 or NaOH were used to obtain three replicate bottles at each of six pH values (Table 5-1). The bottles were incubated in a dark BOD incubator at 20°C (± 1°C) for 170 days to allow a natural senescence and decay of the plants. Samples (∿5 mL) were removed and filtered for SRP analysis about every 10-15 days, and initial and final pH values were measured. The sample volume was not replaced, and a noticeable sulfide odor after 30 days indicated anoxic conditions. Some oxygen was introduced during the sampling process, but the bottles remained unstoppered for a minimal length of time (usually 30 s/bottle).

The second preliminary experiment involved intact, live Eleocharis plants incubated in aerated glass bottles maintained in the dark at pH 3.7, 4.8, or 5.5 (Figure 5-1). Based on the first preliminary experiment, it was not anticipated tht continued pH adjustment would be necessary. However, the pH began to increase in all three groups after 1 month of incubation. After 6 weeks of incubation the pH in all bottles was near 7.0, and the experiment was terminated.

Table 5-1. Initial and final pH values in first preliminary decomposition experiments.

Group	Addition, mL		Initial pH	Final pH
	1 N NaOH	1 NH_2SO_4		
B	2.0		11.50	8.37
C			5.61	3.93
A1		0.02	4.94	4.07
A2		0.20	3.35	4.04
A3		2.0	2.31	2.37
A4		4.0	2.02	2.08

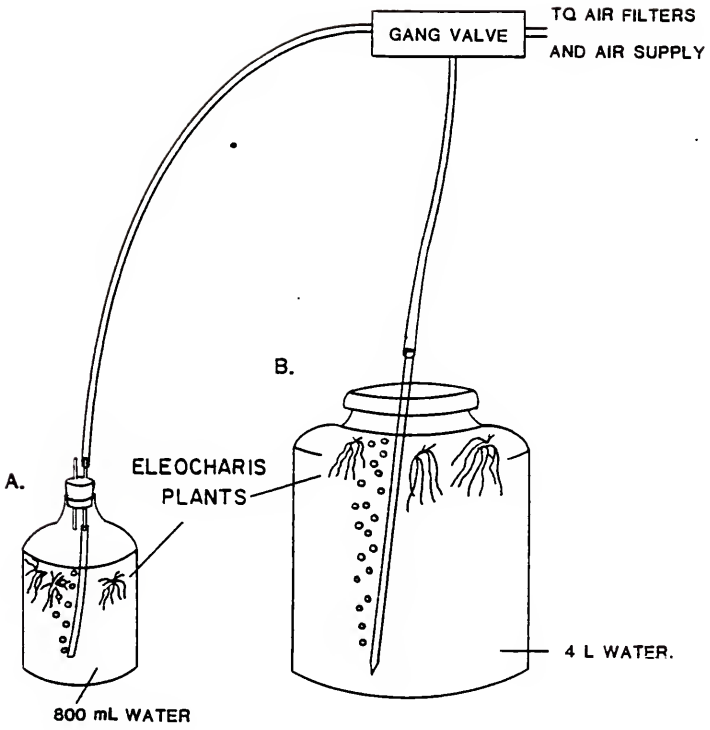

Figure 5-1. Incubation set-ups in aerated decomposition experiments (A. preliminary; B. final).

Final Experimental Design

The final decomposition experiment was carried out under similar conditions. Freshly washed Eleocharis plants were blotted dry and 0.5 g (± 0.01 g) of intact plants were added to each of eight experimental bottles. These 1-gal screw-cap plastic Nalgene bottles were filled with 4 L of lake water that had been passed through glass- fiber filters to remove large particulates while allowing small planktonic forms to be introduced. Additions of 1 N H_2SO_4 or NaOH were used to achieve duplicate bottles at four pH values: 3.7, 4.1, 4.7, and 5.7.

After pH adjustment, the bottles were incubated at room temperature under fluorescent lighting (ambient light-dark cycle) for 1 week to allow the plants and bacterial populations to respond to the new pH conditions. At that time plastic screw caps were installed and the bottles were transferred to a dark storage cabinet. Aeration was provided from a glass pipette inserted through a hole in the cap of each bottle (Figure 5-1), in order to ensure oxygenated conditions and a well-mixed system.

The pH of these systems was checked weekly, and acid or base was added as necessary to maintain the desired pH values. Aliquots were removed periodically for SRP, TP, and TDP analysis using previously described methods. TP and TDP were followed for the first 44 days, and release of SRP was followed for 227 days.

Results and Discussion

Preliminary Experiments

Table 5-1 shows the initial and final pH values in the un-aerated decomposition bottles from the first preliminary experiment. The control group (C) received no pH adjustment; NaOH was used to increase the pH in group B; and the symbols A1 through A4 indicate increasingly lower pH values. The phosphorus content of the Websteria plants was 0.15% initially (Table 5-2).

Figure 5-2 shows changes in SRP in those decomposition bottles during the 170-day incubation period. A rapid initial release (~10 days) of SRP occurred at all pH values except the two closest to the lake pH (Group C, pH 5.6; and Group A1, pH 4.94). This suggests that pH adjustment killed the plants at pH 11.55 (B) and pH <3.35 (A2, A3, and A4), resulting in rapid release of cellular SRP to the water. This release was followed by a period of uptake (to day 41) in A2, A3, and A4, which appears to correspond to an increase in heterotrophic biomass. Those bottles exhibited extensive fungal and/or bacterial growth on the decomposing plants (Table 5-3). SRP in A2 and A3 stayed relatively low during the remainder of the incubation, although it did fluctuate between 10 and 60 μg/L. The lowest pH (A4) showed a second SRP increase after day 41. At the highest pH (B) SRP continued to increase for 55 days, after which the concentration decreased. Nevertheless, SRP was consistently higher than 150 μg/L at the highest pH after day 10.

SRP did not begin to increase in the bottles without pH adjustment (Group C) until day 41, but it reached 100 μg/L by day 94. In the

Table 5-2. Water and phosphorus content of plants used in decomposition experiments.

Experiment	Plant	% H_2O in* fresh wt	n†	mg P/g* dry wt	n†
1st Preliminary	Websteria	93.0 ± 0.4	4	1.45 ± 0.03	4
2nd Preliminary	Eleocharis	89.7 ± 0.8	3	12.86 ± 2.42	8
Final	Eleocharis	88.9 ± 1.1	3	14.82 ± 3.63	9

*Mean ± standard deviation.
†n = number of observations.

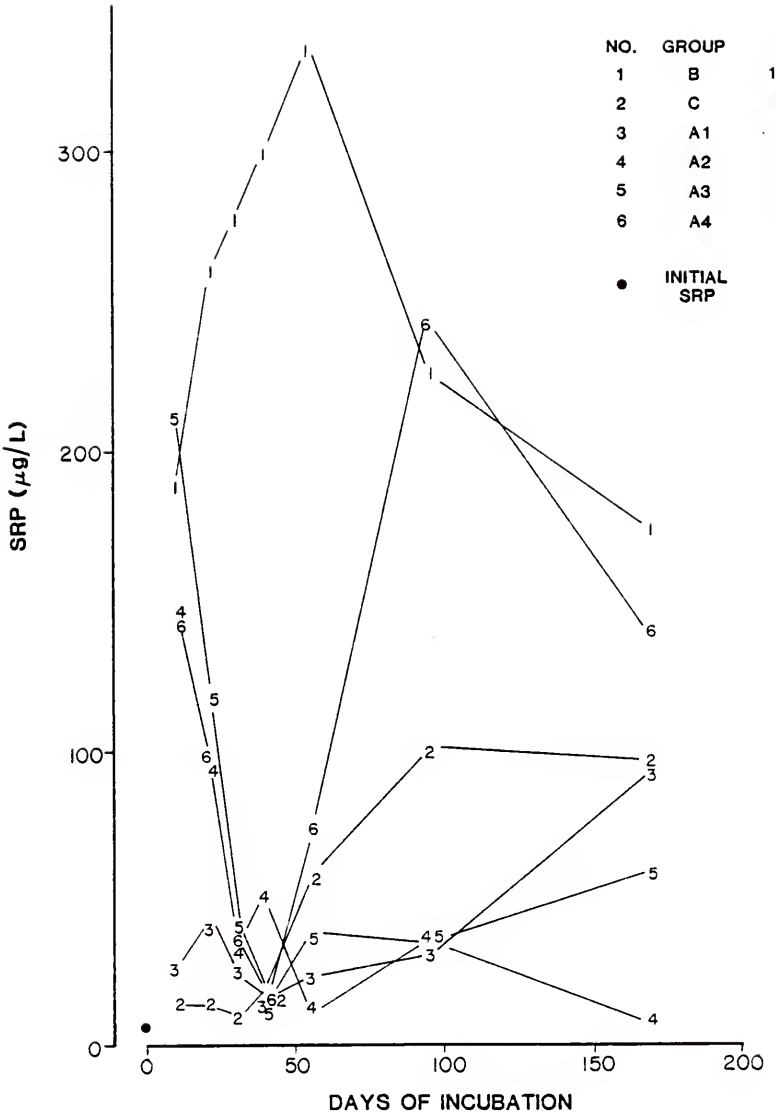

Figure 5-2. Changes in SRP in unaerated decomposition bottles (each point represents the mean of three bottles).

Table 5-3. Qualitative observations during unaerated decomposition of Websteria sp.

Group	Incubation Period		
	21 Days	30 Days	41 Days
B	Plants green, floating; water colored; no odor.	Plants same as Day 21; odor of cut grass.	Plants still green, floating; water colored; odor of hay.
C	Plants pale, on bottom; water turbid, foul (non sulfide) odor.	Plants same as Day 21; bacterial or fungal growths in water; sweetish odor.	Plants appear decomposed; water cloudy; faint, non sulfide odor.
A1	Plants decomposing on bottom; water turbid; strong sulfide odor.	Same as Day 21.	Plants matted; water slightly colored; strong sulfide odor.
A2	Plants brownish, on bottom, covered by mucouslike sheath; strong sulfide odor.	Plants same as Day 21; water clear; strong sulfide odor.	Plant debris covered by bacteria or fungi; water clear or slightly turbid; sulfide odor.
A3	Plants discolored, on bottom; apparent fungal growth; water clear; no odor.	Plants same as Day 21; sour-sweet odor.	Plants matted; water turbid; fungal filaments; faint sweet odor.
A4	Plants discolored, on bottom; apparent fungal growth; water clear; no odor.	Plants same as Day 21; fungal growths; sweetish odor.	Plants appear decomposed, colorless, but not matted; fungi; sweetish odor.

bottles that received the smallest acid addition (A1) SRP release showed a similar delay, and by the end of the incubation SRP also was near 100 µg/L.

The initial total phosphorus in the Websteria plants (Table 5-2) would have yielded 680 µg/L with complete conversion to SRP. Final SRP values represented only 21% and 26% of this potential at the pH extremes (A4 and B), 14% in C and A1, and a mere 1.5% in the A2 group. These results are much lower than those reported by Foree and McCarty (1968), who found that after 200 days of anaerobic decomposition only 40% of the initial particulate phosphorus in cultured algae remained as refractory solids. Extensive growths of bacteria and fungi observed in the Websteria decomposition bottles appear to have reduced SRP release to the water, although the lack of consistent anoxic conditions may have inhibited the decomposition process.

It is interesting to note that the final pH vaues in groups C, A1, and A2 were all close to 4.0, even though initial pH ranged from 3.35 to 5.61 (Table 5-1). There was a net pH decrease in C and A1 during the incubation, and a net increase in A2 during the same period. This phenomenon strongly suggests two concurrent mechanisms in these groups: 1) all of the sulfate added to groups A1 and A2 (as H_2SO_4) ultimately was reduced, resulting in consumption of all of the added H^+; 2) the decomposition process resulted in an equal production of acidity in groups C, A1, and A2.

The lowest pH values (2.02 and 2.31) were too extreme for sulfate reducing bacteria, and thus there was no significant pH increase in those bottles during the incubation. Furthermore, qualitative observations recorded during the incubation also suggest that different

processes occurrred at the different pH levels (Table 5-3). While the bottles adjusted to pH 2.02 and 2.31 exhibited an odor, it was sweetish rather than a sulfide smell. A sulfide odor was noticed in groups A1 and A2, but not in group C (no H_2SO_4 addition). In addition to these differences in odor, there was a trend of increased fungal growth as pH decreased.

These results indicate that decomposition (and phosphorus release) can occur as low as pH 2, although the decomposer organisms and end products may change drastically at such low pH. Since some plants appear to have been killed initially by the acidification while others closer to the lake pH were not, no conclusions can be drawn about the effect of pH on phosphorus release rate during this experiment. However, near the lake pH (roughly between pH 3.4 and 5.6) decomposition seemed to produce acidity, and sulfate reduction apparently consumed essentially all of the H^+ (added as H_2SO_4) necessary to reduce pH from 5.6 to 3.4.

Figure 5-3 shows the changes in SRP concentration during the dark incubation period in the second preliminary experiment, and the corresponding pH values. Significant SRP release occurred in all three treatments. Initial concentrations ranged from 20 to 70 µg/L, and final values were about 400–550 µg/L. Although SRP was consistently and significantly higher ($\alpha < 0.05$) in the low pH treatment than at high pH, the rates of SRP increase were essentially the same.

The pH increases were unexpected because oxidation reactions typically produce acid rather than consuming it (e.g., oxidation of NH_4^+ to NO_3^-, or HS^- to $SO_4^=$). A subsequent test without plants

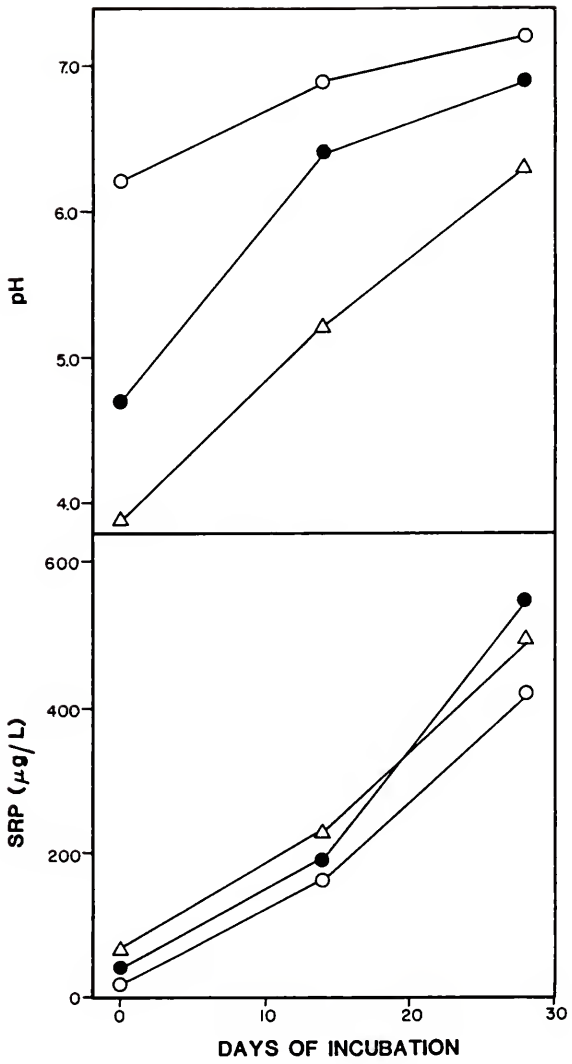

Figure 5-3. Changes in pH and SRP during second preliminary decomposition experiment with Eleocharis.

indicated that the glass incubation bottles were not the source of the observed buffering. Therefore the decomposition process appears to have resulted in a net decrease in $[H^+]$ concentration.

Final Experiment

The final decomposition experiment used a larger water:plant ratio to reduce the effect of this pH increase, and pH was checked and adjusted on a weekly basis to maintain the desired ranges. Figures 5-4 through 5-7 show changes in SRP in duplicate microcosms maintained at four pH values (3.7–5.5) during 227 days of aerobic senescence and decomposition of Eleocharis. Initial SRP concentrations all were less than 5 µg/L, and final values ranged from about 80 to 115 µg/L. Soluble reactive phosphorus values did not differ significantly by pH groups on the last two sampling dates (ANOVA, $\alpha > 0.05$), although the initial release of SRP (50–60 days) tended to be fastest at the lowest pH (Figure 5-8). The bottles maintained at pH 5.5 showed a lag of 30 days in which SRP remained <10 µg/L, while levels increased to 15–40 µg/L at the lower pH values during that same period.

Soluble organic phosphorus (SOP) and POP also were measured during the first 44 days of incubation in this experiment. Soluble organic phosphorus values generally were near 1 µg/L during that period, and never exceeded 5 µg/L. Particulate organic phosphorus concentrations also were low; initial POP was 0–1 µg/L, and levels gradually increased to 3–8 µg/L by day 44. Thus most of the phosphorus released from the Eleocharis plants was SRP, and the lag in SRP increase at pH 5.5 cannot be attributed to a slower conversion of SOP to SRP. Nichols and Keeney (1973) observed an initial release of SOP which preceded an increase in

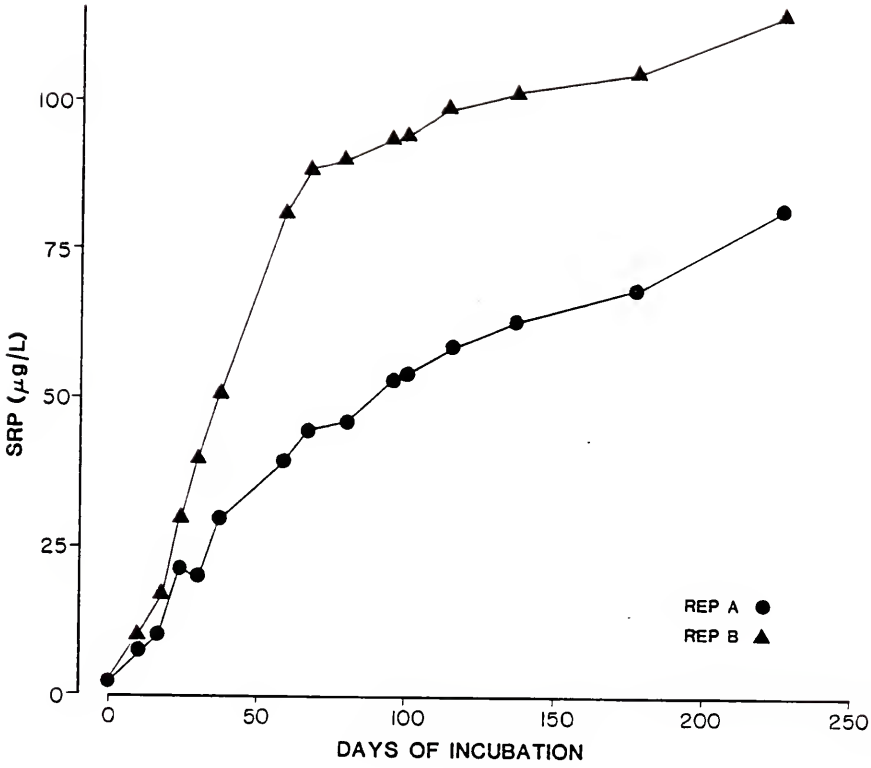

Figure 5-4. Changes in SRP at pH 3.7 during 227-day aerobic decomposition of Eleocharis.

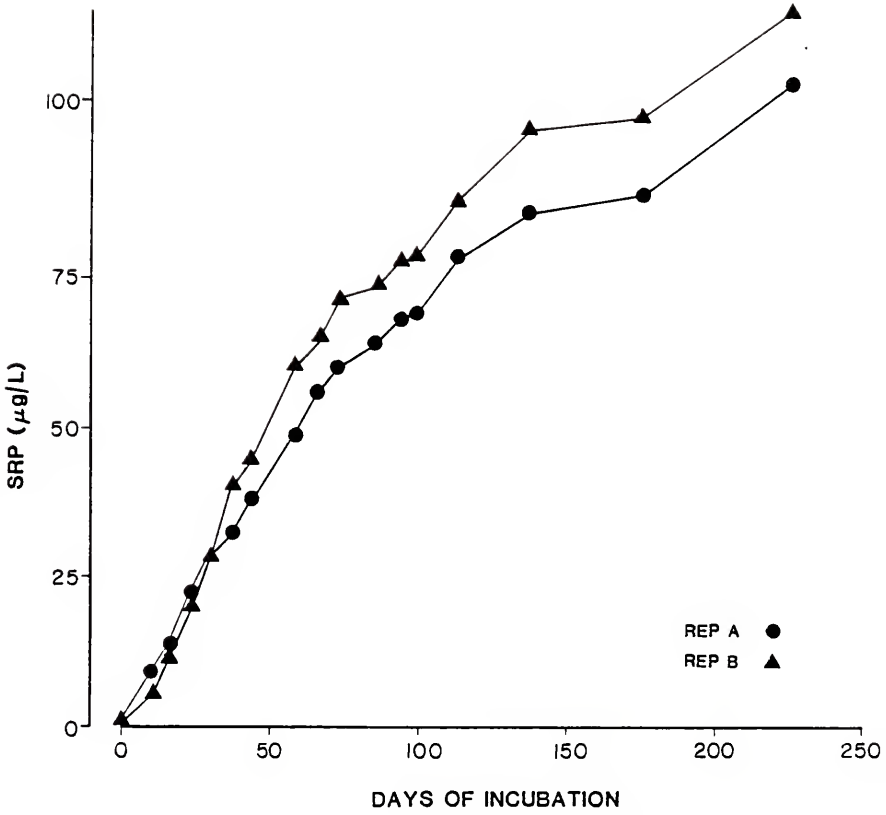

Figure 5-5. Changes in SRP at pH 4.1 during 227-day aerobic decomposition of Eleocharis.

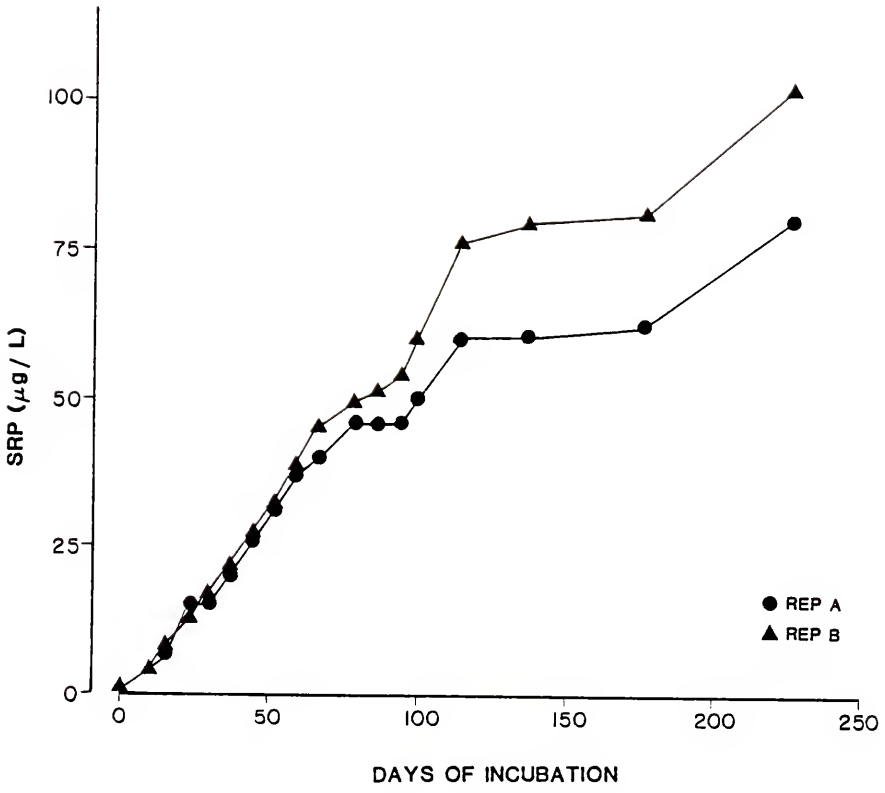

Figure 5-6. Changes in SRP at pH 4.6 during 227-day aerobic decomposition of Eleocharis.

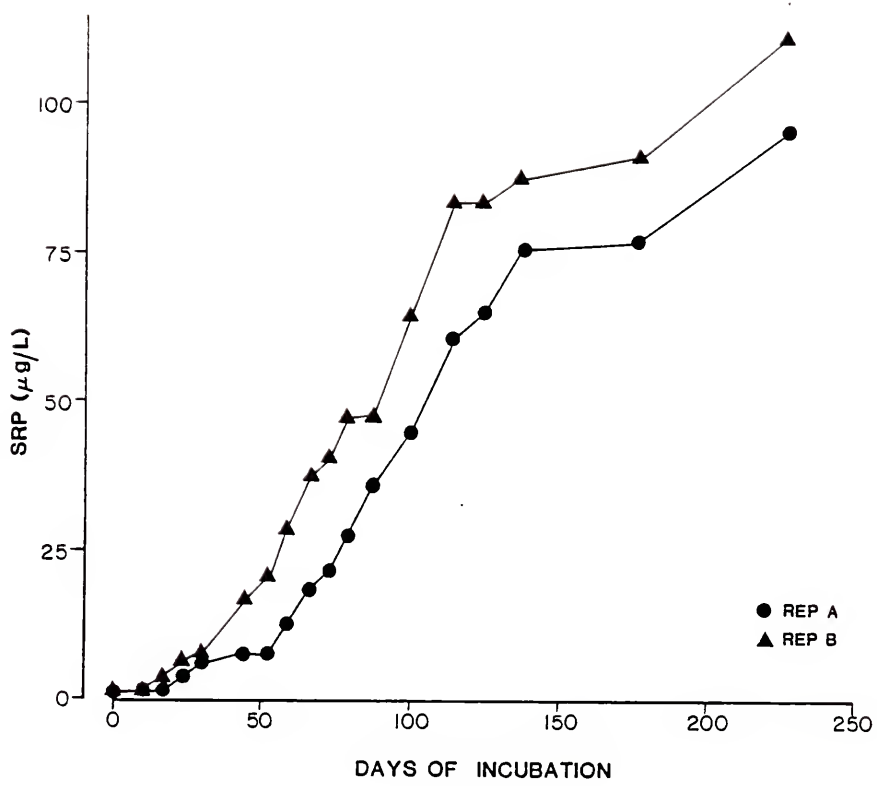

Figure 5-7. Changes in SRP at pH 5.5 during 227-day aerobic decomposition of Eleocharis.

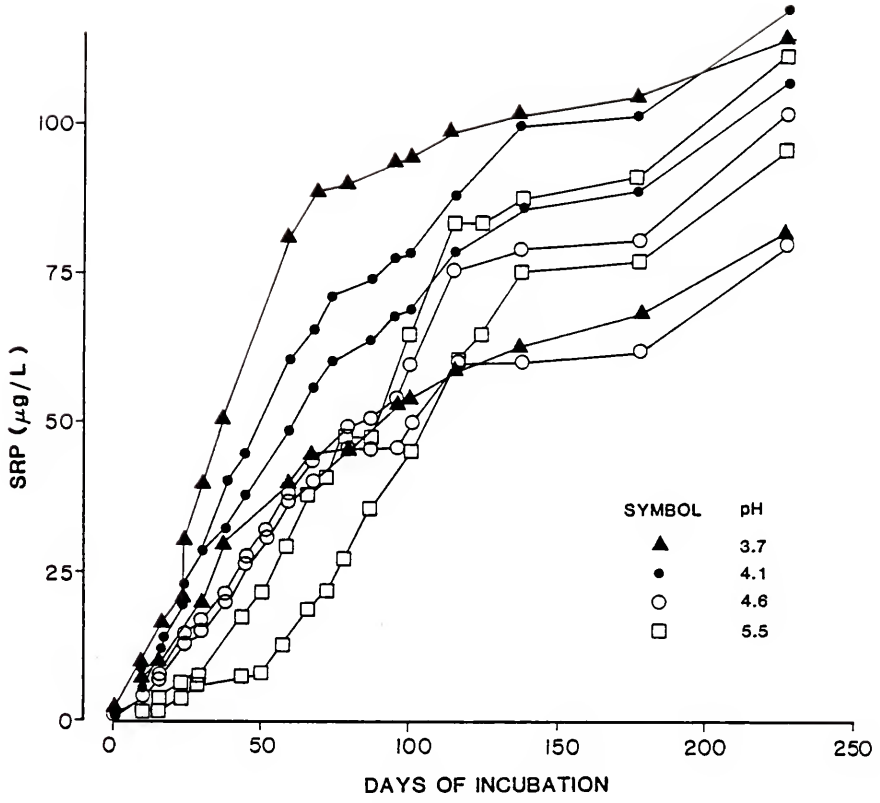

Figure 5-8. Composite of Figures 5-4 through 5-7.

SRP during decomposition of Myriophyllum exalbescens. However, their macrophytes had been killed by herbicide treatment, which would cause a rapid release of the cellular contents (including SOP) before the decomposition process began.

Based on the initial phosphorus content of the Eleocharis plants (Table 5-1), complete decomposition would have resulted in a final SRP concentration of 200 µg/L in the bottles. The observed range of final SRP values (80–115 µg/L) constitutes 40–58% of that potential, which means that 42–60% of initial plant phosphorus remained as refractory particulate material or heterotrophic biomass. These results are consistent with those of Foree et al. (1970), who found that 50% of the initial particulate phosphorus in cultured algae was released during 1 year of aerobic decomposition.

The fate of the remaining 40–60% of original particulate phosphorus in the macrophytes would depend on rates of sediment accumulation and internal sediment processes. Refractory sedimentary materials continue to decompose at slow rates (Foree et al. 1970), and therefore constitute a potential source of phosphorus to overlying water for years after the initial (≈1 yr) period of rapid SRP release.

These experiments demonstrate that the release of SRP from decomposing aquatic macrophytes is not affected by pH (over the range 3.7 to 5.5), and they suggest that other aspects of decomposition are similarly unaffected by low pH. These findings contradict the "oligotrophication" hypothesis of Grahn et al. (1974), but they support the results of many subsequent studies of the effect of acidification on decomposition. Sediment oxygen demand and glucose turnover show no effect of reduced experimental pH (Andersson et al. 1978; Gahnstrom et

al. 1980), while Schindler (1980) found no significant change in TP and no evidence of decreased decomposition during the 3-year experimental acidification of a Canadian lake from pH 6.6 to 5.6.

CHAPTER 6
SEDIMENT-WATER INTERACTIONS

Introduction

Sediment adsorption and release reactions can affect phosphorus concentrations in lake water. The relative importance of these processes in any given lake depends on sediment characteristics, water chemistry, lake morphometry (e.g., ratio of sediment surface to lake volume), and other factors that affect mixing within the lake. This chapter describes the physical and chemical characteristics of McCloud Lake sediments as well as experiments designed to evaluate the effect of pH on the capacity of those sediments to adsorb or release phosphorus. The experimental design included well-mixed batch systems and intact cores of surficial sediment.

Background

Both sediment characteristics and conditions in the overlying lake water have been shown to affect phosphorus adsorption. MacPhearson et al. (1958) found that maximum phosphorus adsorption occurred over the pH range 5.5 to 6.5 with sediments from lakes of several different types, and that more phosphorus was released from the sediments at higher and lower pH values. Other workers have shown greater release

of sediment phosphorus at high pH than at low pH (Andersson et al. 1978; Gahnstrom et al. 1980).

As discussed in Chapter 2, sediment iron and aluminum are important agents in the adsorption of inorganic phosphorus. Surface charge is another sediment characteristic that affects phosphorus adsorption. According to Laverdiere and Weaver (1977), surface charge characteristics of certain soil types are strongly pH dependent. These include highly weathered tropical soils and spodosols, both of which are rich in hydrous oxides of Fe and Al. The sign of the surface charge depends on pH, and the magnitude of the charge at any given pH is determined by the ionic strength of the bulk solution. The authors further described a potentiometric acid-base titration method that can be used to determine the pH at which the sign of the net surface charge reverses (pH_{ZPC}).

Langmuir adsorption isotherms offer an empirical approach to the interpretation of phosphorus adsorption data. The Langmuir equation is derived from theoretical considerations of gas adsorption onto solids, but it is also commonly used to model adsorption of phosphorus onto soils. A linear form of the equation is

$$m/x = 1/Q^{o} + 1/Q^{o}bC \qquad \text{(EQ 4)}$$

in which,

m = weight of dry sediment (g);

x = amount of phosphorus adsorbed (mg);

Q^{o} = maximum adsorption with monolayer coverage (mg P/g dry sediment); and

b = constant that reflects energy of interaction between solute and adsorbent.

Therefore, if experimental data fit the Langmuir model, a plot of m/x versus 1/C should give a straight line with y intercept at $1/Q^o$ and a slope of $1/Q^o b$.

Methods

Sediment Characterization

Surficial mid-lake sediments were collected in July 1983 by compositing replicate petite Ponar grab samples from six widely spaced locations in the open water area of the lake. This composite sample was homogenized and standard procedures were used to determine physical characteristics (APHA 1980). An ashing-HNO_3 digestion procedure (Delfino and Enderson 1978) was used to measure total Fe and Al in the pelagic sediment. Aliquots of the sample also were extracted with 0.1 M Na-pyrophosphate ($NaP_2O_7 \cdot 10\ H_2O$), which has been shown to extract organically bound Fe and Al in soils without dissolving crystalline forms (McKeague 1967). Total and extractable Fe and Al were determined by flameless AAS.

The charge characteristics of the pelagic sediment were evaluated by potentiometric titration (Laverdiere and Weaver 1977). The procedure involved titration of 10 g of soil in 100 mL of 0.01, 0.1 or 1.0 N NaCl with dilute HCl or NaOH. A magnetic stirrer provided constant mixing, and approximately 0.01 meq of acid or base was added at 2-min intervals. To avoid drying the sediment, this procedure was modified by using 50 g wet sediment (3.48 g dry weight) and 50 mL of 0.02, 0.2,

or 2.0 N NaCl. These mixtures were titrated with 0.1 N HCl or NaOH.

Batch Adsorption/Desorption Experiments

Short (∿1 wk) incubations of well-mixed sediment-water systems were used to evaluate the potential of McCloud littoral and mid-lake sediments to adsorb or release SRP over the pH range 3.5-7.0. For the first experiment (June 1982), a sediment sample was composited from four petite Ponar grabs collected in littoral areas (0.5-1.0 m depth) free of macrophytes. Aliquots (25 g wet weight) of this homogenized sample were added to 100 mL of membrane-filtered (0.45 µm) lake water in 30 125-mL screw-cap polyethylene bottles. Solution pH was measured after shaking for a 1-day equilibration period and 0.1 N H_2SO_4 or 0.1 N NaOH was added to obtain six replicates at each of five pH values over the desired range. Solution pH was measured again after 2 more days of mixing, and 1 mL of a stock KH_2PO_4 solution (to give 1 mg/L in 100 mL of water) was added to three replicates in each pH group. After 5 more days of mixing, final supernatant pH values were measured, and a solution sample from each bottle was filtered through a 0.45 µm membrane filter. SRP was determined for the filtered supernatant samples and the initial filtered lake water on an AutoAnalyzer II system.

Similar procedures were used with pelagic sediments. A mid-lake surface sediment composite sample was collected as previously described (six locations) in February 1983. It was homogenized, and 50-g (wet weight) portions were mixed with 200-mL aliquots of membrane-filtered (0.45 µm) lake water in 48 250-mL screw cap polyethylene bottles. Twenty additional bottles (used as controls) contained only 200 mL of the filtered lake water with no sediment. After an initial equilibration

period (1 day) and pH check, 1 N solutions of NaOH and H_2SO_4 were used to obtain eight sediment-water replicates at five pH values over the range of 3.5 to 6.9. The remaining eight sediment-water bottles gave four replicates at each of two intermediate values in the same pH range. Four control replicates (water only) were titrated to each of the five pH values represented by eight sediment-water replicates, and no controls were used at the pH values with only four sediment-water replicates. After another day of shaking for equilibration to the new pH conditions, control and experimental flasks at each pH were spiked with four levels of stock SRP solution: 0.0, 0.5, 1.0, and 2.0 mg P/L above the ambient equilibrium SRP concentration. The final experimental matrix was as follows:

	pH						
	3.5	3.8	4.2	4.7	5.5	6.4	6.9
No. Sediment-Water Bottles/SRP Level	2	2	2	1	2	1	2
No. Controls/SRP Level	1	1	1	0	1	0	1

After 2 days of mixing, final solution pH and aluminum and SRP concentrations were measured.

Undisturbed Core Experiments

Well-mixed batch systems can demonstrate the potential of a lake's sediments to adsorb or release phosphorus, but the extreme experimental

conditions make it difficult to extrapolate the result to the ambient lake situation. Therefore undisturbed sediment cores were used to simulate more closely phosphorus adsorption and release in McCloud Lake.

Sixteen cores consisting of ∿10 cm undisturbed mid-lake sediment and ∿30 cm of overlying lake water were collected manually using SCUBA equipment and pre-cut lengths of clear cellulose acetate butyrate tubing (4.13 cm ID) stoppered with parafilm-covered rubber stoppers. Disturbance of the interface was minimal, as indicated by clarity of the overlying water, and the presence of chironomid tubes and filamentous algal growth at the sediment surface when the cores were raised to the boat. The cores were transported carefully to the laboratory, where they were installed upright in a wooden rack covered with black plastic to exclude light. The volume of overlying water was adjusted to 400 mL, and the tubes were covered with parafilm to minimize evaporation. Each core was aerated through a small glass pipette inserted to about one-half the depth of the water column. Aeration provided vertical mixing of the water without suspending sediment, and maintained an oxygenated water column (anoxic conditions have not been detected in the McCloud Lake water column).

After the cores had been allowed to equilibrate for 3 days, 0.1 N H_2SO_4 or NaOH additions were used to obtain four replicate cores at water column pH values 3.7, 4.1, 4.7, and 6.0. Sediment consumption of H^+ and OH^- necessitated pH measurement and acid or base addition every 2–3 days to maintain water column pH within $\pm$0.2 units of the nominal value. After 1 month of pH adjustment, SRP was added to two cores in each pH group to increase water column concentration by 1 mg P/L. Controls consisted of one aerated tube with 400 mL lake water

adjusted to each pH and the same SRP spike. Water column SRP concentrations in the spiked cores were followed to evaluate the effect of pH on the capacity of undisturbed lake sediment to adsorb phosphorus. In addition, periodic SRP measurements in all replicates during the 1-month pH adjustment, and in the unspiked cores after that, provide an estimate of pH effects on SRP release from undisturbed sediments.

Results and Discussion

McCloud Sediment Characteristics

Sediments in the littoral area of McCloud Lake are distinctly different from those in the open-water part of the lake (Table 6-1). The flocculent, highly organic profundal sediments are fine textured and homogeneous. Littoral sediments, however, are more variable in texture and composition. Wave action in some areas has exposed alternating layers that are predominated by sand or coarse, peaty organic matter. The nature of the littoral sediment surface depends on which layer is exposed in any particular area. Total Fe and Al (Table 6-1) were comparable to values reported from similar lakes in this area (Thompson 1982) and the organically bound fractions represented about 30% (Al) and 50% (Fe) of respective totals.

Theoretical considerations indicate that at the pH_{ZPC}, surface potential and surface charge of constant potential surfaces will be zero. At pH values other than the pH_{ZPC}, the magnitude of a positive or negative surface charge will vary with salt concentration, while at the pH_{ZPC}, net charge will be independent of ionic strength. Figure 6-1 shows the results of the potentiometric titration

Table 6-1. Some physical and chemical characteristics of McCloud Lake sediments.

	Sediment	
	Littoral	Profundal
Water, Percent	68.7	93.3
Volatile Solids, Percent Dry Weight	11.6	77.7
Sand, Percent Dry Weight	18.3	0
Total Al, Percent Dry Weight	--	2.0
Extr. Al, Percent Dry Weight	--	0.57
Total Fe, Percent Dry Weight	--	0.36
Extr. Fe, Percent Dry Weight	--	0.18
Interstitial Al, mg/L	--	0.078
Interstitial Fe, mg/L	--	0.025

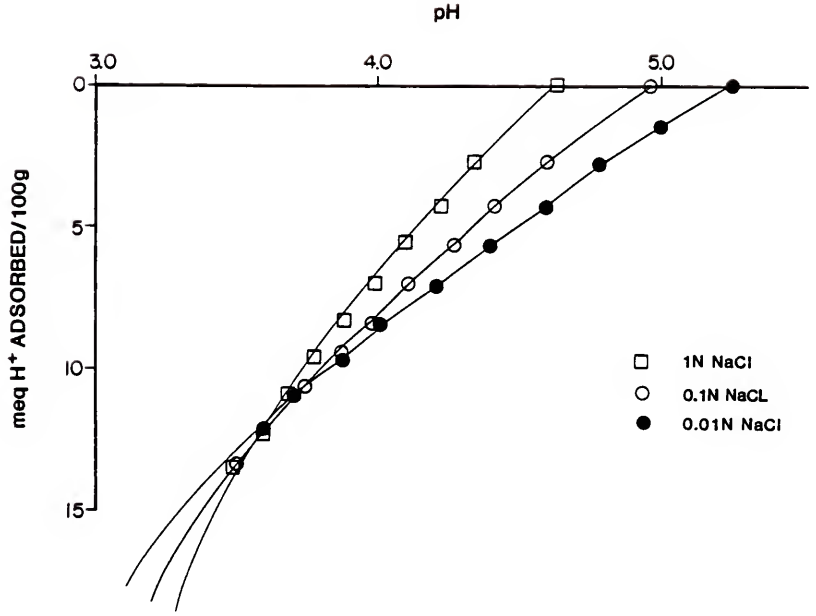

Figure 6-1. Potentiometric titration of McCloud mid-lake sediment (in NaCl solution) with 0.1 N HCl.

of mid-lake sediments. The three titration curves intersect at a unique pH value (pH_{ZPC}) that is indenpendent of electrolyte concentration and locates the point at which the net surface charge reverses. Although the pH_{ZPC} is not precisely identified, it does occur in the pH range 3.5 to 3.7. Laverdiere and Weaver (1977) pointed out that highly organic soils often have low pH_{ZPC} values, and noted that the occurrence of pH_{ZPC} below the zero point of titration (no acid or base addition) indicates the presence of a permanent negative charge on the surface. McCloud sediments thus appear to have a low pH_{ZPC} because of their high organic content, and they display a permanent negative charge that is independent of pH. Net charge does not become positive until solution pH is $\sim$3.6 or lower.

Batch Adsorption/Desorption Experiments

Table 6-2 summarizes the results obtained in the batch experiment using littoral sediments. No significant release of SRP from the sediments occurred over the pH range 3.5 to 6.7. SRP adsorption ranged from 6.8 to 11.9 µg P/g dry sediment, which constituted a removal of about 55% to 95% of the added SRP. The effect of solution pH on the amount of SRP adsorbed can be seen in Figure 6-2. Maximum adsorption occurred at pH 4.4, and only slightly less was removed at other pH values between 3.5 and 4.4. Adsorption decreased markedly at pH values above 4.4.

Table 6-3 presents the results obtained in batch experiments with profundal sediments. The amount of SRP adsorbed per gram dry sediment increased as the initial concentration increased, although at a given pH value the percent of added SRP retained stayed relatively constant.

Table 6-2. SRP adsorption/release by littoral McCloud sediments.

pH Group	SRP Added, mg/L	Final SRP, g/L*	Sediment Dry Wt, g	SRP Adsorbed	
				g P/g dry wt	% Added P
3.5	1.0	88 ± 27	8.02	11.2	89.7
3.8	1.0	60 ± 5	8.01	11.6	93.0
4.4	1.0	43 ± 2	8.02	11.9	95.0
5.5	1.0	156 ± 15	8.02	10.2	81.7
6.7	1.0	388 ± 36	8.02	6.8	54.6
3.5	0	1.0 ± 1.7	8.01		
3.8	0	0.0 ± 0.0	8.02		
4.4	0	4.0 ± 1.7	8.01		
5.5	0	3.6 ± 0.6	8.01		
6.7	0	3.0 ± 0.0	8.02		
Initial SRP in filtered lake water	-	3.0 ± 0.6			

*Mean ± standard deviation.

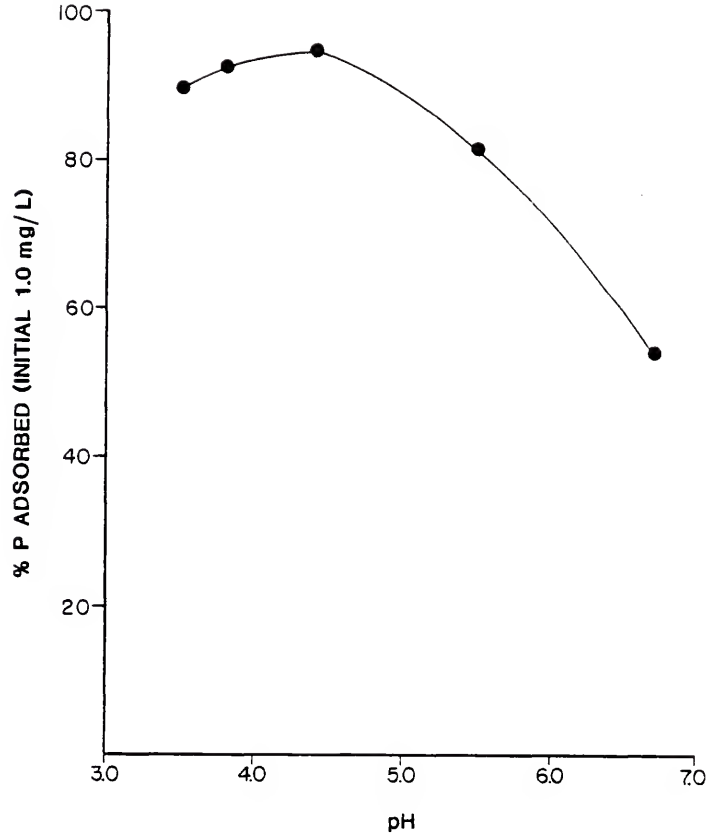

Figure 6-2. Effect of pH on SRP retention by littoral McCloud Lake sediments.

Table 6-3. SRP adsorption/release by profundal McCloud sediments.

pH Group	SRP Added, mg/L	Final SRP, g/L*	Sediment Dry Wt, g	SRP Adsorbed	
				g P/g dry wt	% Added P
3.5	0	6 ± 1	4.04		
	0.51	23 ± 4	3.97	29.2	95.5
	1.02	45 ± 1	3.98	60.1	95.5
	2.03	97 ± 1	3.97	117.6	95.2
3.8	0	0.5 ± 0.7	3.97		
	0.51	8 ± 0	3.97	30.3	98.4
	1.02	16.5 ± 0.7	3.97	61.9	98.4
	2.03	38 ± 6	3.98	125.0	98.1
4.2	0	0 ± 0	3.97		
	0.51	7.5 ± 0.7	3.98	30.3	98.5
	1.02	13 ± 1	3.97	62.5	98.7
	2.03	40 ± 9	3.98	123.0	98.0
4.7	0	0	3.97		
	0.51	3	3.98	31.3	99.4
	1.02	11	3.97	62.3	98.9
	2.03	42	3.96	123.6	97.9
5.5	0	0 ± 0	3.97		
	0.51	5 ± 1	3.98	31.1	99.0
	1.02	22.5 ± 2	3.98	61.5	97.7
	2.03	103 ± 4	3.98	119.0	95.0
6.4	0	16	3.98		
	0.51	43	3.96	28.9	91.6
	1.02	136	3.98	54.4	86.6
	2.03	680	3.96	84.0	66.5
6.9	0	20 ± 1	3.99		
	0.51	217 ± 4	3.99	18.0	57.4
	1.02	480 ± 13	3.99	33.0	52.7
	2.03	1290 ± 0	3.97	46.0	36.5
Initial SRP in filtered lake water		2 ± 0.7			

*Mean ± standard deviation.

Adsorption ranged from 33 to 62.5 µg P/g dry sediment in the group with ∿1 mg/L SRP addition, which amounted to 53% to 99% of added SRP. The range of percent SRP removal was similar for both littoral and profundal sediments, although adsorption per gram dry sediment was about five times higher for the profundal sediment. This difference appears to be related to the higher organic content of profundal sediments, which suggests that the organic fraction is largely responsible for SRP adsorption by McCloud sediments. When removal is normalized to organic content, the littoral SRP adsorption range is 58.6 to 102 µg P/g dry organic sediment, and the corresponding profundal (1 mg/L added SRP) range is 43 to 80.5 µg P/g dry organic sediment.

The effect of pH on SRP adsorption by profundal sediments (Figure 6-3) was very much like the pattern seen for littoral sediments. Maximum removal occurred at pH ∿ 4.7. At lower pH values adsorption decreased slightly, while above pH 4.7 the decrease was much more extreme. In bottles that received no addition, final SRP concentrations showed a similar but opposite effect of pH (Figure 6-4a). The low initial SRP concentration (2 µg/L) was reduced below detectable levels between pH 4.2 and 5.5, while release from the sediment occurred at pH 3.5 and at pH 5.5.

Two possible mechanisms for the observed effect of pH on sediment SRP adsorption include changes in sediment characteristics with pH (e.g., surface charge) and changes in SRP speciation with pH. Theoretical considerations indicate both processes could influence anion adsorption. As mentioned previously, most surfaces have a net negative charge under normal environmental conditions. For constant potential surfaces, decreases in pH reduce the magnitude of this net charge until

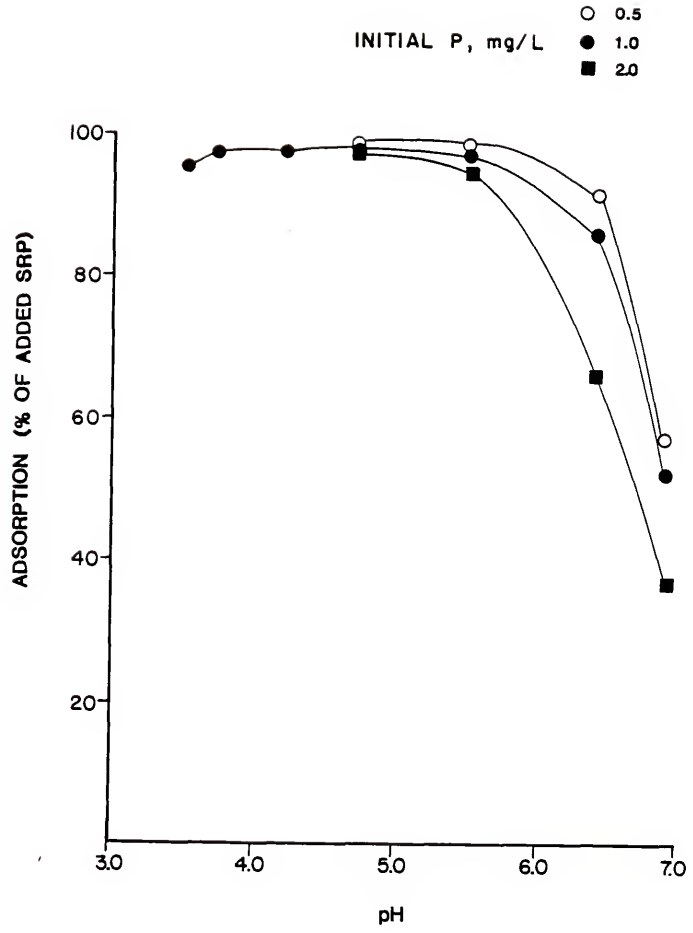

Figure 6-3. Effect of pH and initial concentration on SRP retention by profundal McCloud Lake sediment.

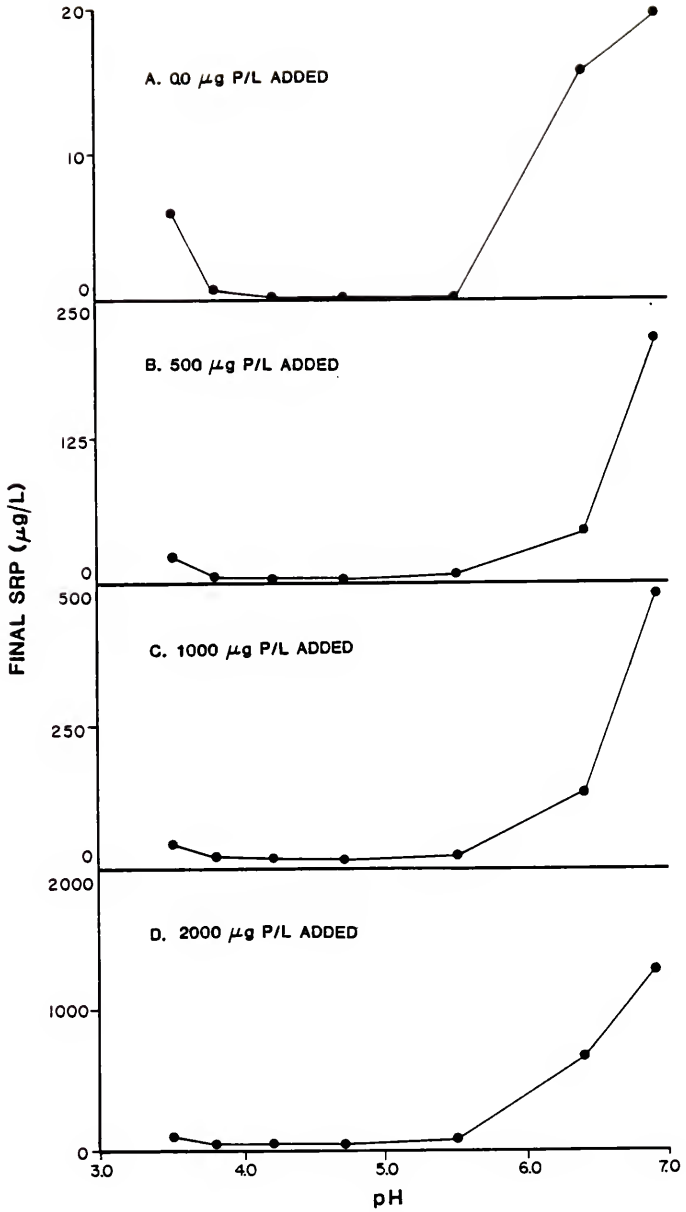

Figure 6-4. Effect of pH on SRP release or adsorption by McCloud Lake profundal sediments.

the pH_{ZPC} is reached, at which point further reduction in pH increases the net positive charge. Anion adsorption thus should show a continual increase as pH is reduced, within limits imposed by the solubility and physical characteristics of the solid surface. SRP adsorption by McCloud sediments, however, reached a maximum at about pH 4.5 and decreased at lower pH values.

Sediment charge characteristics can explain the observed effect of initial concentration on the percent SRP removed (Figure 6-3). At a given pH $\leq$4.2, the percent added SRP that was adsorbed was independent of initial SRP concentration (within the range 0.5 to 2.0 mg P/L). As pH increased above 4.2, however, percent SRP removal showed an inverse relationship to initial concentration, and this effect became more pronounced as pH increased. Figure 6-1 shows that near the sediment pH_{ZPC} (3.5 to 3.8), ionic strength of the bulk solution did not affect surface charge, but as pH increased above pH_{ZPC}, a higher ionic strength caused a more negative net surface charge. Since the phosphorus addition was as a salt (KH_2PO_4), larger SRP additions resulted in higher ionic strength bulk solutions (and thus a greater net negative surface charge), which reduced the capacity of the sediment to adsorb SRP as pH increased above ZPC.

Solution pH also has a minor effect on the distribution of ionic species of SRP over the pH range 3.0 to 7.0, as shown in Figure 6-5. $H_2PO_4^-$ predominates over the entire range, with small proportions of undissociated H_3PO_4 at low pH and $HPO_4^=$ at higher pH values. Hingston et al. (1967) demonstrated that $H_2PO_4^-$ is the species most readily adsorbed, and its distribution corresponds remarkably well to the pattern of phosphate adsorption by littoral and pro-

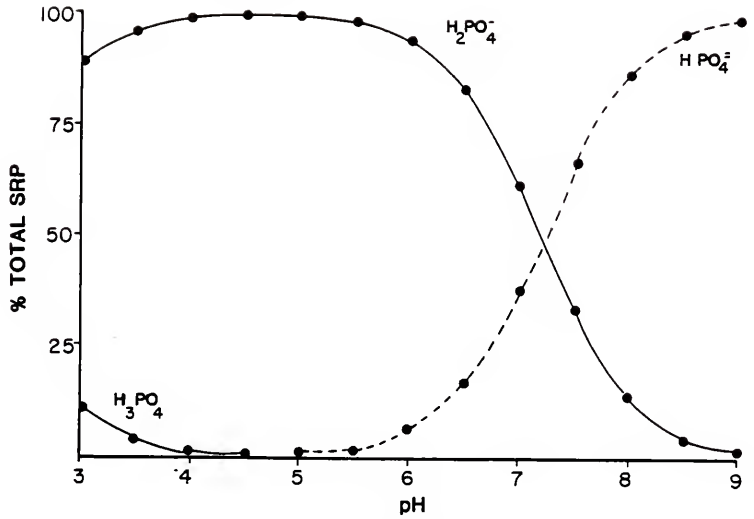

Figure 6-5. Effect of pH on speciation of SRP.

fundal sediments (Figure 6-6). Over much of the experimental pH range, the profundal sediment removed essentially all of the added $H_2PO_4^-$. Deviations at higher pH values occurred because of generally increasing net negative surface charge and because of increasing ionic strength effects on surface charge. Littoral sediments removed a smaller percentage of the available $H_2PO_4^-$, but this was probably because of their lower organic content. The pattern of SRP release by profundal sediments shows the same relationship to changes in SRP speciation. No SRP release occurred over the pH range in which $H_2PO_4^-$ constitutes ~99–100% of SRP_T, but SRP was released at higher and lower pH values.

Table 6-4 summarizes the regression parameters and isotherm coefficients that were obtained by applying the Langmuir equation (EQ 4) to data from the phosphorus adsorption experiment using mid-lake sediment. A limited number of data points was available for these calculations since only three levels of phosphorus addition were used. Data for the two pH values without duplicate bottles (4.7 and 6.4) were not included because each offered only three data points. Although the scarcity of data points dictates caution in interpreting these results, the data do seem to fit the Langmuir equation fairly well; regression r^2 values ranged from 0.943 to 0.997.

Values of Q^o represent theoretical maximum adsorption of phosphorus with monolayer coverage of the solid surface. The three lowest pH values showed the highest Q^o values, while the pH 5.5 value was intermediate and the lowest Q^o was at the highest pH. This trend reflects again the pH effect seen in phosphorus adsorption at specific levels of phosphorus addition.

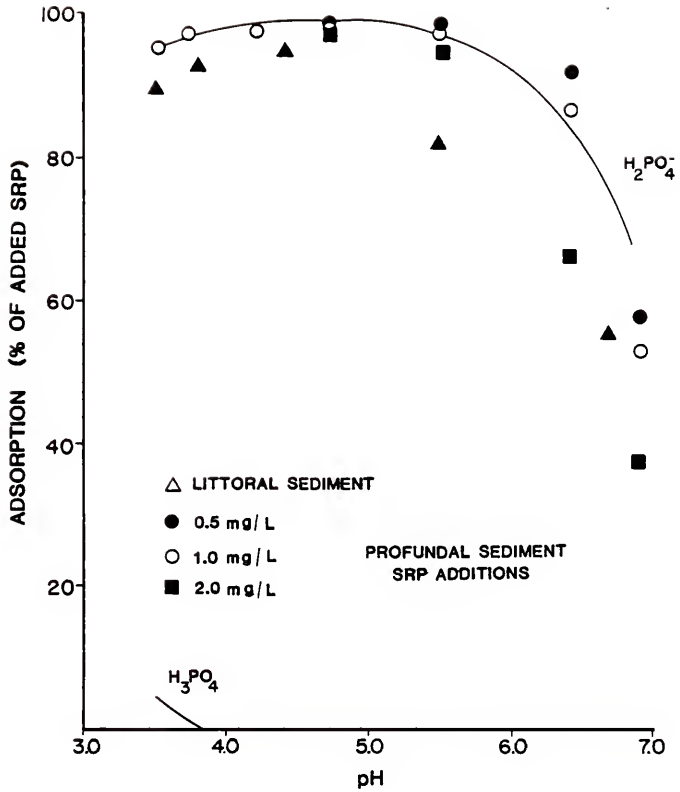

Figure 6-6. Composite of Figures 6-2, 6-3, and 6-5.

Table 6-4. Regression parameters and isotherm coefficients obtained from Langmuir isotherm plots of mid-lake sediment phosphorus adsorption data.

pH	Regression, r^2	Slope	Intercept	Q^o, mg/g	b, L/mg
3.5	0.943	0.70	1.58	0.633	2.26
3.8	0.997	0.25	1.47	0.680	5.88
4.2	0.950	0.22	1.53	0.653	6.95
5.5	0.980	0.15	8.13	0.123	54.8
6.9	0.988	8.97	13.49	0.074	1.50

Sediment Core Experiments

Results obtained with the undisturbed sediment cores were similar in some respects to trends seen with the batch systems. Figure 6-7 shows mean water column SRP concentrations in the unspiked cores over a 46-day period after desired nominal pH values were attained. Average SRP concentrations varied in the range of 4 to 14 µg/L, but no consistent pH-related trend was evident. Based on results of the batch incubations, the columns maintained at the pH extremes (3.7 and 6.0) would have been expected to exhibit the highest SRP values. This was not the case. However, several differences in experimental conditions possibly account for the fact that the low pH columns showed relatively low SRP concentrations. First, SRP release from undisturbed sediment should be slower than from well-mixed sediment because of decreased sediment-water contact. Secondly, while the complete system (sediment and water) was titrated to the desired pH in the batch experiments, only the water column and an unknown depth of sediment were affected in the cores. Finally, during the longer incubation of the cores, biological activity could have been sufficient to mask a physical or chemical pH-mediated release of SRP from the sediments. The cores were incubated in the dark to eliminate the influence of primary producers, but no effort was made to control heterotrophic activity. Bacterial and fungal growths were observed on the tube walls; zooplankters were observed in some water columns; and, as mentioned earlier, chironomids were present at the sediment surface of some cores.

Figure 6-8 shows the removal of SRP from solution in the spiked cores and controls. Some initial loss of SRP occurred in the controls, but over the 30-day period, this loss amounted to only 10% to 16% of

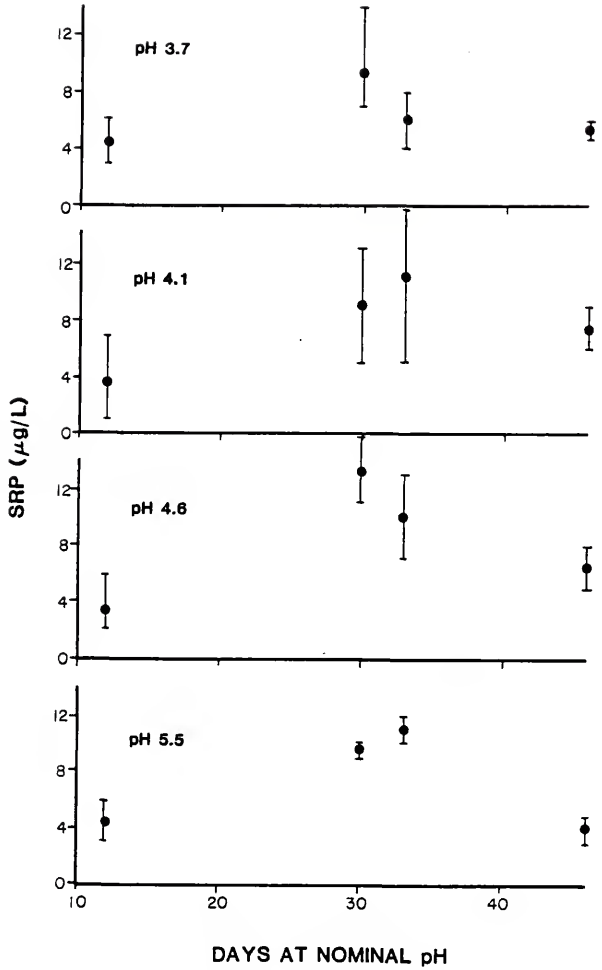

Figure 6-7. SRP variation in unspiked cores (means and ranges).

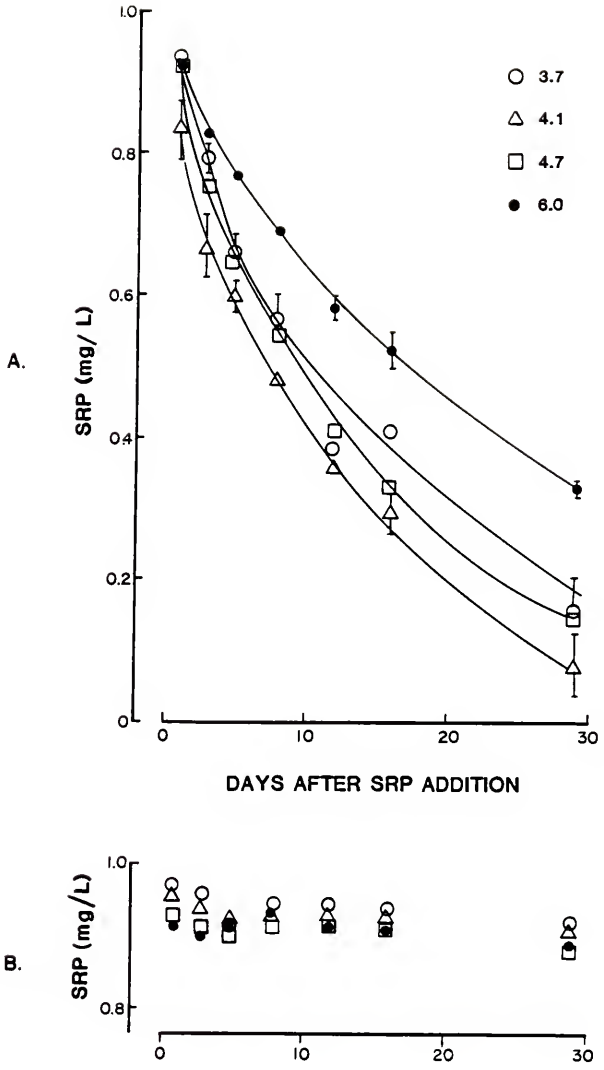

Figure 6-8. SRP concentration in spiked sediment-water columns (A) and controls (B).

the phosphorus adsorbed in the sediment-water columns. The effect of pH on phosphorus adsorption in these cores was similar to the trends seen in the batch adsorption experiments. The rates of SRP disappearance seemed to be influenced by $H_2PO_4^-$ distribution. Phosphorus removal was slowest in the cores maintained at pH 6.0, and fastest in the pH 4.1 cores, while intermediate adsorption rates were obtained in the cores at 3.7 and 4.7.

The curves in Figure 6-9 indicate that first-order kinetics can be used to model adsorption by the cores. Empirical rate constants (k) obtained from the slopes of regressions of the natural logarithm of SRP versus time are given in Table 6-4. They range from 0.036/day to 0.090/day and mirror the pH trend seen in Figure 6-8. Analysis of covariance (ANCOVA) demonstrates that there are significant differences among the slopes (k values) of the four regression equations, and further ANCOVA comparison shows that the rate constants for cores at pH 3.7 and 4.7 are not significantly different ($\alpha = 0.81$). However, those rate constants do differ significantly from the k values obtained for the cores at pH 6.0 and 4.1 ($\alpha < 0.05$). The net result is the following relationship among the four rate constants:

$$k_{4.1} > k_{3.7} = k_{4.7} > k_{6.0}.$$

The rate of phosphorus adsorption is fastest at pH 4.1; slightly slower at pH 3.7 and 4.7; and slowest at pH 6.0. This trend is similar to the pH effect seen in SRP adsorption in the batch experiments. Further reduction of pH in McCloud Lake thus could increase slightly the rate of phosphorus adsorption onto sediments, but the most dramatic change in adsorption rate would occur over the pH range 4.7 to 6.0.

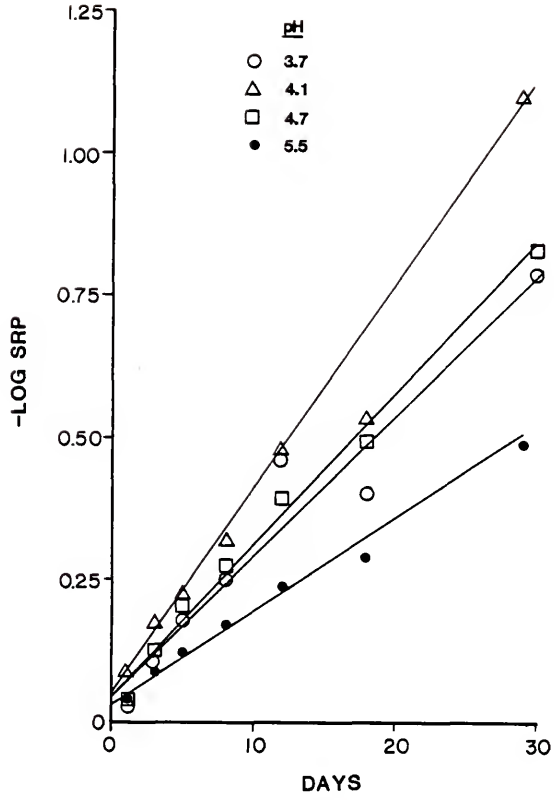

Figure 6-9. First-order SRP uptake plot for sediment-water columns.

Table 6-5. Phosphorus adsorption rate constants for undisturbed sediment cores.

Core pH	Rate Constant, day^{-1}	Regression, r^2
3.7	0.061	0.93
4.1	0.090	0.86
4.7	0.063	0.97
6.0	0.036	0.99

In summary, pH does affect adsorption of phosphorus by littoral and pelagic McCloud sediments, and the same pH trends are seen in well-mixed or undisturbed sediment-water systems. Amounts of phosphorus adsorbed and rates of adsorption vary only slightly between the present pH of the lake ($\sim$4.7) and pH 3.5. Compared to the magnitude of variation possible in other processes that affect phosphorus concentrations in lakes, the differences in adsorption over this pH range seem insignificant. However, as pH is increased above approximately 5.0, phosphorus adsorption decreases significantly with sediments from McCloud Lake. This implies that the effect of pH on phosphorus adsorption may contribute to the observed trend of low TP values in acidic lakes by increasing rates of phosphorus removal as lakes are acidified over the pH range 7.0 to 5.0.

CHAPTER 7
SUMMARY AND CONCLUSIONS

Laboratory and *in situ* experiments as well as an examination of the historical data base were used to characterize phosphorus dynamics in acidic, soft-water McCloud Lake and to evaluate the effect of acidification on phosphorus cycling processes. The lake presently exhibits nutrient and chlorophyll-*a* concentrations typical of oligotrophic Florida lakes. A 15-year decline in pH from 4.85 to 4.55 has not been accompanied by significant changes in TP, chlorophyll-*a*, or nitrogen to phosphorus ratios, which indicate phosphorus-limited primary production.

Total phosphorus and SRP both show maximum levels during late spring and summer. These variations appeared to be related to rainfall patterns and lake levels during 1980–1982. Rainfall to the lake surface contributes 90% of the water input to McCloud Lake, and atmospheric phosphorus deposition approximates loading rates required to maintain mesotrophic conditions. This emphasizes the importance of atmospheric nutrient loading to small lakes similar to McCloud Lake, but it also suggests that low pH may contribute to the low TP in the water column of McCloud Lake.

Rooted submergent macrophytes constitute a significant in-lake storage of phosphorus that is approximately 2.5 times the average water column phosphorus storage. These plants appear more likely to mobilize sediment phosphorus than to compete with phytoplankton for water column

phosphorus, although periphytic algae may limit the impact of mobilized phosphorus on phytoplankton.

In situ littoral and open-water mesocosms indicated that acidification (from 4.6 to 3.7) does lead to reduced water column TP values, although the trends were not consistent in the open-water enclosures. The pH treatments did not affect chlorophyll-a concentrations or phytoplankton densities. However, copepods were almost eliminated at pH 3.7 in littoral and open-water enclosures. No relation was seen between pH and rates of phosphorus uptake by mesocosm seston. Laboratory microcosms similarly showed no consistent relation between pH and the activity of extracellular acid phosphatase enzymes.

The amount of phosphorus released from decomposing submersed macrophytes was independent of pH (over the range 3.7 to 5.5) after 227 days of aerobic dark incubation. Initial rates of release were somewhat faster at the lowest pH, although it was not established whether this was due to a difference in the times required for the plants to die (live, intact plants were used). Nevertheless, these experiments indicated that acidification does not inhibit phosphorus release during decomposition of organic matter, as suggested by Grahn et al. (1974).

Adsorption of phosphorus by McCloud Lake sediments was affected by pH, apparently through changes in the charge characteristics of the sediment surfaces and, to a lesser extent, by pH-controlled changes in SRP speciation. Maximum phosphorus adsorption occurred near pH 4.7 with littoral and profundal sediments, although adsorption rates and amounts varied only slightly between pH 5.0 and 3.5. However, phosphorus adsorption decreased significantly as pH was increased above approximately 5.0. This suggests that the effect of pH on retention of

phosphorus by sediments may contribute to the observed trend of low TP values in acidic lakes. The effect would be most dramatic over the pH range 7.0 to 5.0, and further acidification of lakes near the pH of McCloud Lake would have little effect on phosphorus adsorption.

Of the processes investigated in this study, only sediment adsorption demonstrated a response to pH that is consistent with a reduction of TP levels in acidic lakes. Sedimentation rates measured in McCloud Lake were high, but the effect of pH was not evaluated. Similar phosphorus adsorption experiments with sediments from many additional lakes would demonstrate the extent of the phenomenon and would clarify the significance of the process to reduced TP in acidic lakes. A more detailed measurement of the phosphorus budget terms in McCloud Lake (total phosphorus deposition instead of wet only; seepage phosphorus inputs) would help clarify the relation between phosphorus loading to the lake and its trophic status.

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BIOGRAPHICAL SKETCH

Reuben Walter Ogburn, III, was born and raised in Mobile, Alabama. He obtained a B.S. in Biology from Southwestern at Memphis in June 1970 and entered active duty in the U.S. Navy in September of that year. During his 2-year tour as an electronics technician aboard the U.S.S. Shelton (DD-790), he visited several countries in the western Pacific Ocean and saw combat duty off the coast of North Vietnam. After an Honorable Discharge from the Navy, he returned to Alabama to enter an M.S. program in Marine Science at the University of Alabama. Walt and the former Marlyn Wadley were married in 1974, and he obtained the M.S. in 1976. The Ogburns were Peace Corps Volunteers in Talcahuano, Chile, where Walt taught Marine Ecology and Intertidal Ecology at the Catholic University of Chile from 1976 to 1978. Their first son, Reuben Walter Ogburn, IV, was born in Concepcion, Chile, in 1977. After they returned to the U.S., Walt worked as a hydrographer/biologist for an environmental consulting firm in Mobile, Alabama, until 1980, when he entered the Ph.D. program in the Environmental Engineering Sciences Department at the University of Florida. A second son, Douglas Rayfield Ogburn, was born in Mobile in 1980. Walt has worked for Breedlove Associates, Inc., a Gainesville consulting firm, since August 1983.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Joseph J. Delfino, Chairman
Professor of Environmental Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Adjunct Professor of Environmental Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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